AN INVESTIGATION OF USING ISOCHORIC DATA POINTS IN THE DEVELOPMENT OF NATURAL GAS EQUATION OF STATE

A Thesis

by

AOUBAI MAHMOUD KHAZNDAR

Submitted to the Office of Graduate and professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Kenneth R. Hall
Co-Chair of Committee,	Mert Atilhan
Committee Members,	Marcelo Castier
	Michael Fraim
Head of Department,	Nazmul Karim

May 2014

Major Subject: Chemical Engineering

ABSTRACT

Access to energy is essential for the survival of humans, and the need for energy rises continuously because of population increase and economic progress. Fossil fuels continue to play the major role in satisfying energy demand. Among the fossil fuels, natural gas is the cleanest, most available, and most useful of the energy sources. It finds extensive use in residential, commercial, electric power generation and industrial applications. Moreover, the international energy outlook report released in 2011 indicates that yearly world natural gas consumption should increase from 111 trillion cubic feet in 2008 to 169 trillion cubic feet in 2035. Recently, new natural gas reservoirs have been discovered in many places throughout the world. In 2012, the total world supplies of proved natural gas reserves were estimated to be 6,746.8 trillion cubic feet. Thus, studies on natural gas are significant to advance the technique of natural gas processing, transportation and storage. In these three sectors, an accurate knowledge of the thermodynamic properties of natural gas is essential for engineering and technical processes. Developing accurate equations of state is important, and can provide us with accurate thermodynamic properties for natural gas. In addition, developing new techniques to produce mathematical models is important to create more accurate results and to enrich this field with new ideas, which might provide progress in the future. The aim of this thesis is to demonstrate a new approach for developing an equation of state.

This technique relies upon isochoric data of carbon dioxide pure component to develop mathematical models. This thesis contains nine models based upon experimental

and generated data. The generated data come from REFPROP, which also provides an accurate means to adjust experimental data to true isochores. Within this thesis, a regression analysis was performed - using Polymath 6.1 - to provide mathematical structure of the equation for carbon dioxide. Results indicate that models covering vapor phase has less deviation than models covering liquid or both phases, and models developed by the generated data has less deviation than models developed by the experimental data. The deviation obtained by most of the models was less than the random error imposed upon the data. In this study, we conclude that modeling an equation of state from isochores appears to provide sufficient advantages to encourage additional studies on pure fluids and multi-component mixtures.

DEDICATION

To my parents, family
and country

ACKNOWLEDGMENTS

I would like firstly to thank Texas A&M University for launching a master degree of chemical engineering field in Texas A&M Qatar branch, and for providing an excellent research facilities for graduate students. I would like to extremely thank Dr. Kenneth Hall for giving me the opportunity to work in this project. I thank him for the time he spent, for his patience, and for being nice and helpful always. I am grateful to Dr. Kenneth Hall for financially supporting me during my second year of Ms degree, and for making it possible for me to obtain my degree at Texas A&M University at Qatar.

I would like to thank the very close faculty member to my heart, Dr. Mert Atilhan. I appreciate his help and support both personally and academically. I thank him for his comments and advices on technical aspects.

I would like to express my thanks to Dr. Marcelo Castier for being a committee member, and for helping me modify my results. I thank Dr. Michael Fraim for being a committee member, and for his time and valuable comments.

I would like to express my sincere thanks to all faculty members in the department, and on top of them Dr. Bruce Balmer, the head of chemical engineering department.

I would like to thank all my fellow collogues for the nice time we spent, and for the continuous challenge in academics.

Finally, I would like to thank and dedicate this work to my parents, brothers and sisters. I would have never succeeded without their support, advices, and help. I thank them all from the bottom of my heart.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

1.1 Energy Outlook

It is clear that energy is important for human kind to maintain high standards of living, and to attain significant economic progress. Energy also is necessary to evolve health, education, and social welfare systems, in both developed and developing countries. [1]Because of that, new supplies of reliable and affordable energy from different resources should take place to meet this raising demand. At the same time, concerns about energy supply and its possible impact on the environment has become one of the critical issues which influence the human life. That provides us with variety of energy supply options, energy prices, energy efficiencies and environmentally benign technologies. [2]

Many people around the world have no access to electricity, and several billions of people still use basic fuels such as wood for cooking and heating purposes. In other words, energy resources are one of the top priorities which all people require.

According to the International Energy Outlook study released in September 2011 [3], the world energy consumption grows by 53 percent from 2008 to 2035 (Figure 1.1). Total world energy use rises from 505 quadrillion Btu in 2008 to 619 quadrillion Btu in 2020 and 770 quadrillion Btu in 2035. Much of the growth in energy consumption occurs in non-OECD (non- Organization for Economic Cooperation and Development) countries, where the big demand is a result of the economic growth methodology those

counties implement. In many OECD and non-OECD countries, the energy consumption increases daily.

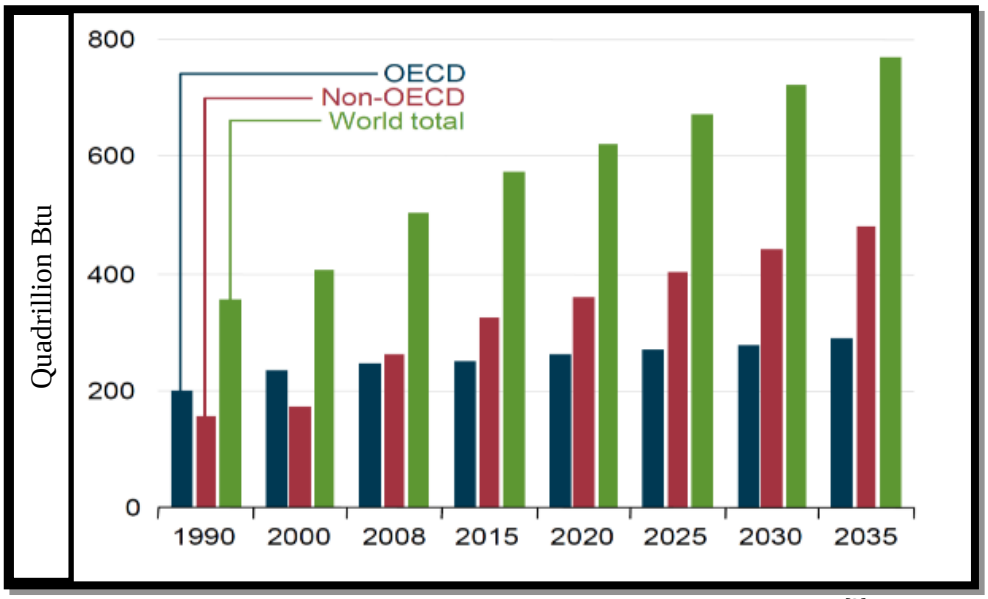


Figure (1.1): World energy consumption from 1990 to 2035 [3]

If we consider the US for instance, energy information administration of the US Department of Energy (DOE) reveals a notable difference between consumption and production of energy over the last fifty years in the US [4]. The US consumed more energy than it produced (Figure 1.2). In 2010, total consumption of energy in the US was 97 Quadrillion Btu, whereas the total production was 78 Quadrillion Btu. In this case, US had to import the need of energy to cover energy demand. Therefore, the US economy had a huge dependence upon fuel exporting countries for price and supply stability. [5] However, in the recent years fossil fuel production has increased significantly in the US to cover almost 100% of energy demand by domestic energy suppliers. [6,7]

Most, if not all of the world regions have encountered this issue. Population is increasing continuously, and the need for energy resource has become a serious and significant issue. Addressing this situation requires diverse range of energy sources including non-fossil fuels and efficient technologies should be available to meet the energy demand. Fossil fuel, however, will continue to play the major role in satisfying the energy demand. Oil, gas and coal have been and will continue to be the most widely used fuels, and have the capacity needed to meet global demand, making up about 80 percent of total energy consumption in 2040. Studies show that natural gas will grow fast enough to overtake coal, to be the second most used fossil fuel in the entire planet after oil. Demand for natural gas will rise by more than 60 percent through 2040. [8]

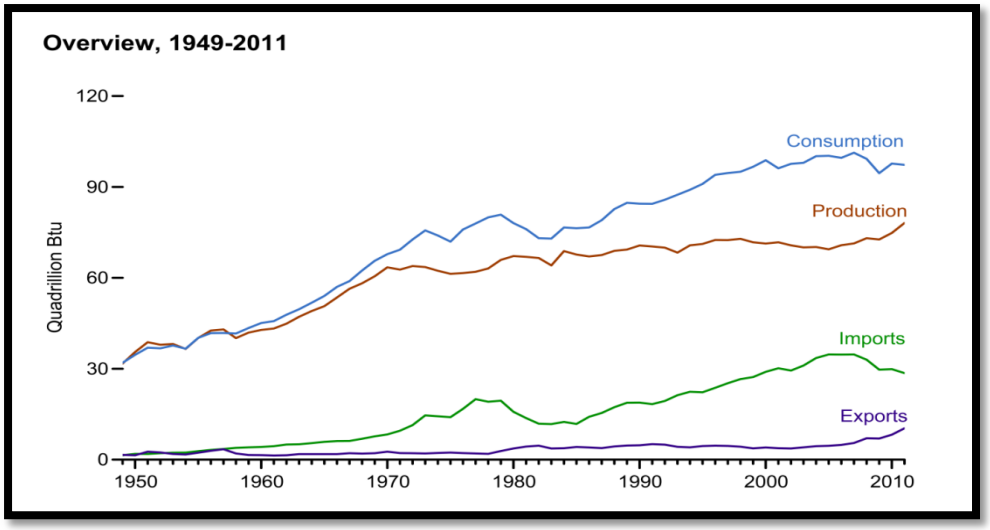


Figure (1.2): Primary Energy Overview in the US [4]

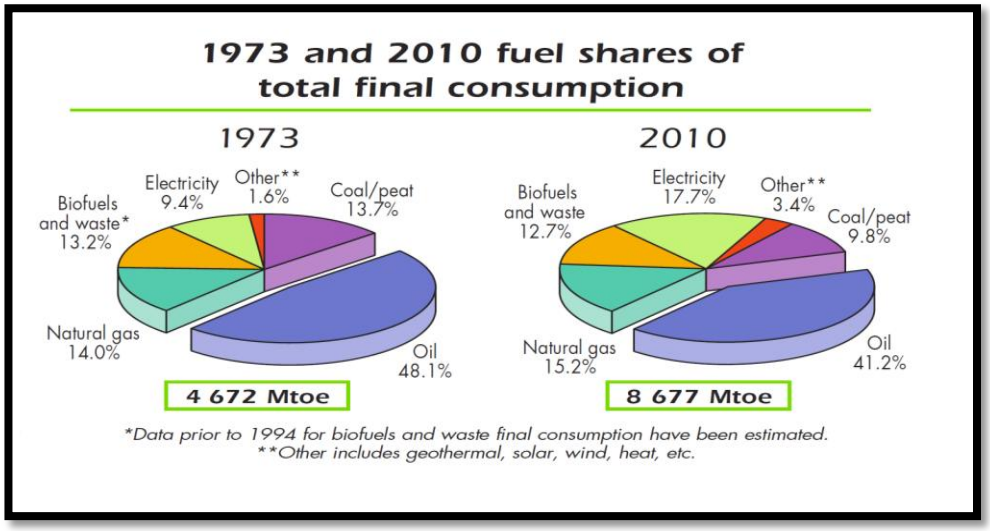


Figure (1.3): 1873 and 2010 fuel shares of total final consumption [9]

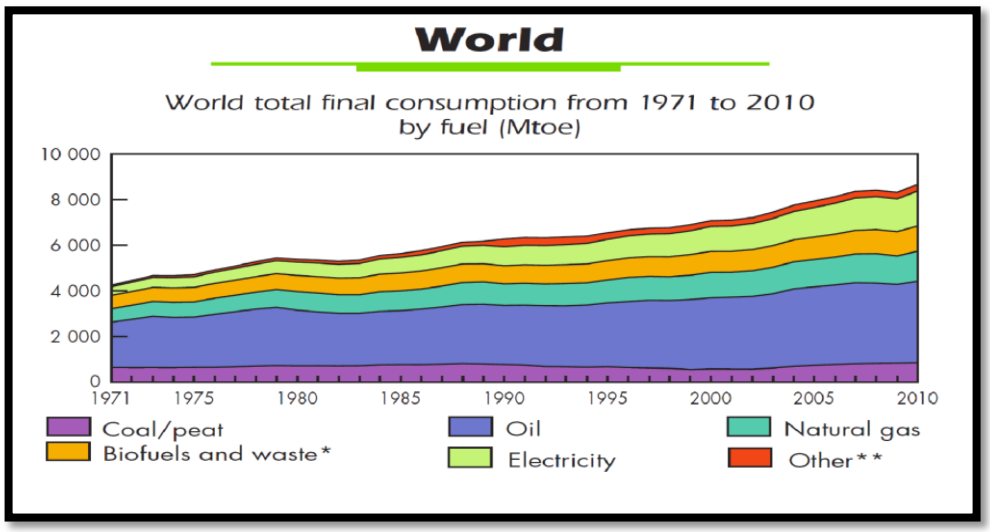


Figure (1.4): World total final consumption from 1971 to 2010 by fuel (Mtoe) [9]

Figures (1.3) and (1.4) show the consumption increase of coal, oil, natural gas and other energy sources, from 1971 to 2010. It is clear that world need for energy is increasing day by day, and natural gas consumption has reached 15.2% of the total energy consumption rate (8677 Million tons of oil equivalent) in 2010. It can be noted that electricity consumption of energy passes natural gas of the total consumption. However, natural gas can still be considered as the second fossil fuel, after oil, because most of the electricity generated is produced by natural gas.

1.2 Natural Gas Overview

Natural gas is among the cleanest, safest, and most useful of all energy sources. It is used extensively in residential, commercial, electric power generation and industrial applications, and it is the most common energy source used for home heating with about 55 percent of American homes using gas. [10] If we compare natural gas to oil or coal, it is definitely more environmentally friendly, it has higher heating value, and it is by far more economical than other energy resources.

Natural gas is a mixture of methane and other paraffinic hydrocarbons such as ethane, propane, butane, pentane etc. and with smaller quantities of nitrogen, carbon dioxide, and non-hydrocarbon gases such as helium, hydrogen sulfide and water [11]. Compositions of natural gas components vary as a function of depth, because of temperature and pressure gradients in the formation. The light hydrocarbons can be extracted easier and faster than heavy ones [12].

World natural gas consumption in 2012 grew by 2.2 % compared to 2011. Consumption growth was below average in all regions except North America, and that is

mainly because of the low price of natural gas in the US. Global natural gas production grew by 3.1 % in 2012. The US recorded the largest volumetric increase of 7.7 %, and remained the world's largest producer. Natural gas output also grew rapidly in Qatar (+25.8%), Russia (+3.1%) and Turkmenistan (+40.6%), more than offsetting declines in Libya (-75.6%) and the UK (-20.8%). [13]

The international energy outlook report 2011 indicates that world natural gas consumption will increase from 111 trillion cubic feet in 2008 to 169 trillion cubic feet in 2035 (Figure 1.5). The major projected increase in natural gas production occurs in non-OECD regions, with the largest increments coming from the Middle East (an increase of 15 trillion cubic feet between 2008 and 2035).

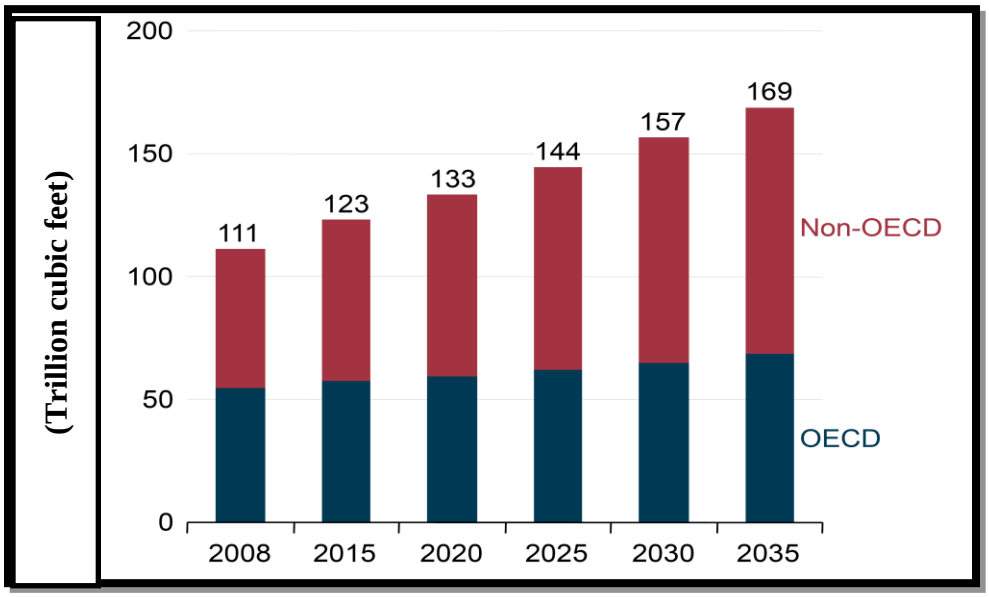


Figure (1.5): World natural gas consumption, 2008 to2035 [3]

In the US, natural gas is mostly used in industry. From 1950 to 2010, natural gas use by sector was fluctuating. However, it was least used for transportation purposes and

most used in industry. Each country has it is own use by sector for natural gas depending upon its proprieties.

Based upon scientific research and studies, demand for natural gas will rise in the future due to the wide utilization in electric power generation and due to the CO_2 emissions concern. By 2025, natural gas – which emits up to 60 % less CO_2 than Coal, when used for electricity generation – will overtake coal to become the second most popular fuel, after oil. The demand is expected to grow in every part of the world, especially in the Non OECD countries, where demand might triple over the next 30 years.

In the near future, the need for natural gas will increase due to many reasons. One of the major reasons is the massive natural gas reserves that the earth possesses. In 2012, the total world proved natural gas reserves were estimated to be 6,746.8 trillion cubic feet. [14]It can be noted by the statistical review of world energy that natural gas reserves in the Middle East only can reach almost 40 % of the total natural gas reserves in the whole world. Russia, Iran, and Qatar have the largest natural gas reserves in the world respectively. The three of them have combined reserves that correspond to about 50% of the world total natural gas reserves as of 2012. Reserves in the rest of the world are distributed fairly evenly on a regional basis. From the statistics of natural gas reserves, we can notice that OECD countries have only 658.4 trillion cubic feet, whereas non- OECD countries have 5,955.7 trillion cubic feet. That means, most of OECD countries rely on importing natural gas from rich countries. Qatar is one of the Middle East countries that hold a substantial role in natural gas reserves.

1.3 Qatar Role of Natural Gas

Qatar is the third country after Russia and Iran in terms of the amount of natural gas proved reserves (Figure 1.6). [15, 16] It has a fundamental role in natural gas export sector as well. Qatar comes second after Russia in exporting natural gas, and it comes fourth in natural gas producers after Russia, US and Canada. So, it is clear how big role Qatar has in natural gas among the world countries compared to its size.

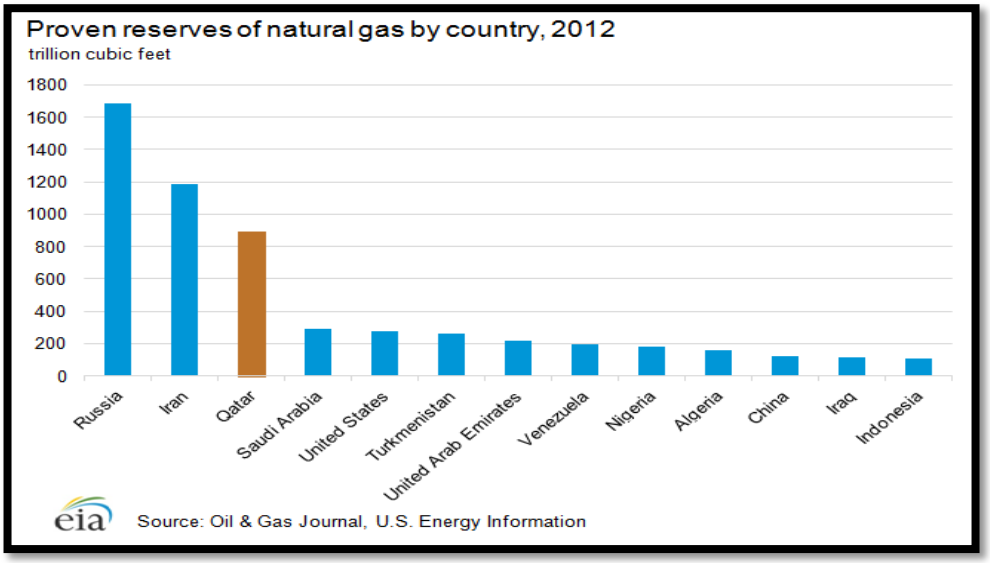


Figure (1.6): Proven reserves of natural gas by country, 2012. [15]

Qatar recently has increased its natural gas production to become one of the key players in the Middle East region in terms of natural gas capacity, because of the abundance of gas in the North Field of Qatar. From 2008 to 2035, Qatar will grow its natural gas production [17] making an increase of 5.4 trillion cubic feet, followed by Iran (5.3 trillion cubic feet of new production) and Saudi Arabia (2.3 trillion cubic feet).

The total natural gas consumption in the Middle East will double from 2008 to 2035, growing by an average of 2.7 percent per year. And that can be a consequence of the regional industrial sector in the Middle East which remains the most important natural gas consumer and will account for 55 percent of total gas use in 2035. This increase of natural gas consumption can be attributed to the big LNG and GTL projects that exist in this region. Qatar more than doubled its LNG liquefaction capacity over the last 7-years and more than doubled its fuel use in LNG liquefaction plants. [18, 19]

In addition to the two GTL facilities (Oryx and Pearl) that are located in Qatar. The Oryx plant consumes 120 billion cubic feet of natural gas per year and produces 30 thousand barrels of different liquid products daily. Whereas, the Pearl project ,the world's largest GTL plant, consumes 660 billion cubic feet of natural gas per year, and produces 140 thousand barrels of liquids per day, including diesel, naphtha, and kerosene. Net exports of natural gas from the Middle East have increased from 1.8 trillion cubic feet in 2008 to 4.8 trillion cubic feet in 2035. Since 2009, Qatar has been the largest LNG exporter in the world. [20] Its total LNG export capacity reached 77 million tons (3.6 trillion cubic feet) per year in early 2011. That is the total capacity of six –mega- sized liquefaction trains. Each train has the capacity to produce the equivalent of 0.36 trillion cubic feet of natural gas per year for export. [21, 22] Qatar's natural gas exports will grow by an estimated average of 12.5 % per year from 2008 to 2015.

1.4 Importance of Thermodynamic Properties Data of Natural Gas

An accurate knowledge of the thermodynamic properties of natural gas mixtures, as well as of their pure components is essential for engineering and technical processes. This requires property calculations that can describe the behavior of a pure fluid and mixture in the homogenous gas, liquid, and supercritical regions, and also for vapor liquid equilibrium (VLE). [23] But, the first step in property calculations is to measure thermodynamic properties in the lab. Since it is impossible to measure all the thermodynamic properties of all systems in nature, we rely upon mathematical models to extrapolate the available experimental data.[24]To develop high standard mathematical models we need to get very accurate (P-ρ-T) data of natural gas components in the lab. This mathematical model is called an equation of state (EOS). In natural gas field, equation of state can help predict the thermodynamic properties of technical applications such as: processing, transportation (through pipelines or by shipping), and storage.

In natural gas processing, fractionation units separate the hydrocarbon components in a series of columns in order to meet pipeline quality and for some commercial specifications. Methane is firstly separated in de-methenizer column, to produce an overhead stream composed of C_1, C_2, and N_2, and lower stream with heavier hydrocarbons that get separated as well in the subsequent sections. That is done in order to use some of them in pre-cooling, liquefaction, and sub-cooling cycles and to produce natural gas liquids (NGL = C5+) and liquefied petroleum gas (LPG).[25-28] This kind of operation is highly dependent upon natural gas equation of state and vapor liquid equilibrium data. In Liquefied natural gas (LNG) transportation, gas volume can be

considerably reduced to about (1/600) of its volume by cooling to about -160 °C at atmospheric pressure, and in this state LNG can be transported easily across oceans. Thus, equation of state is very helpful in this process. Furthermore, retrograde condensation can be encountered in natural gas transportation. [29] Knowing an accurate thermodynamic properties of natural gas can avoid retrograde condensation phenomenon. In operations, vapor-liquid equilibrium data helps avoid condensation of heavy components and P-ρ-T data helps in the design of pressure vessels and heat exchangers and in some operations such as separation and dehydration. Equation of state can provide information about thermal and caloric properties of natural gases and mixtures of natural gas components. In liquefied natural gas storage tanks, knowing thermodynamic properties can be helpful ensuring an excellent condition of health, safety and environmental factors. In addition to that, knowing accurate thermodynamic properties of natural gas can avoid hydrate formation in the pipeline. Basically, hydrate formation happens in the pipelines when temperature decreases rapidly at high pressure with a presence of moisture in the natural gas stream. This can cause serious problems like plugging the pipelines. Hydrate formation can be suppressed by either increasing the temperature of the gas by insulating the pipeline, lowering the pressure or by lowering the dew point of water by adding polar solvents such as methanol or glycols. Thus, knowing an accurate P-ρ-T data can help us avoid hydrate formation. [30-31]

Among P-ρ-T data, density can be considered as the most difficult and important property to measure, because of the need for natural gas custody transfer.[32-33]Accurate density measurements is essential in the gas pipeline transportation to measure the

amount of gas being transferred accurately. A good model should predict an accurate density data for pure and multi-component mixtures. In natural gas mixture systems, the density can be calculated from the equation of state knowing the temperature, pressure and composition. By comparing density predictions to the experimental density measurements, the equation of state can be more reliable. Detailed characterization method (AGA8-DC92) equation of state is an example of mathematical models that are applicable to natural gas mixtures. It was developed by the American Gas Association (AGA), and has been validated against a databank of experimentally measured compressibility factors. GERG 2008 is another example of a powerful natural gas model. It is explicit in the Helmholtz free energy as a function of density, temperature, and composition. And it covers the liquid phase, gas phase, supercritical region, and vapor liquid equilibrium regions for natural gas multi-component mixtures.

1.5 Motivation of the Project

In the natural gas EOS development field, many people use constant temperature (isothermal) data. But, very few people work with constant density (isochoric) data. Experimentally, obtaining isothermal data points is easier and less time consuming. However, the isochoric density derivative is possibly more useful than isothermal derivative. Fitting the isochoric slop is much easier than fitting the isothermal slop. The first and second derivative of isotherms and isochores can be derived from equation (1.1) which is obtained from first law of thermodynamics. Dividing this equation by dV obtains the isochores, and dividing it by dT obtains the isotherm.

$$dA = -SdT - PdV \quad \text{(1.1)}$$

1st derivative: Isochore $(\frac{\partial A}{\partial T})_V = -S$.……..….(1.2)

1st derivative: Isotherm $(\frac{\partial A}{\partial V})_T = -P$…….……..……..…..…. (1.3)

2nd derivative: Isochore $\left(\frac{\partial^2 A}{\partial T \partial V}\right) = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V = -\left(\frac{\partial P}{\partial T}\right)_V$ ……..……..…. (1.4)

2nd derivative: Isochore $\left(\frac{\partial^2 A}{\partial T^2}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial T}\right)_V\right]_V = -\left(\frac{\partial S}{\partial T}\right)_V = -\frac{C_V}{T}$……..…..…. (1.5)

2nd derivative: Isotherm $\left(\frac{\partial^2 A}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T$ …….…….....….....…. (1.6)

A is Helmholtz energy, and S is the entropy. We can notice form the derivatives that the second derivative of isotherm in equation (1.6) obtains the slop of isotherm. And the second derivative of isochore with respect to temperature and volume in equation (1.4) obtains the slop of isochore. The slop of isochore is much easier to fit than the slop of isotherm. Whereas, the second derivative of isochore with respect to temperature in equation (1.5) obtains –Cv/T. Cv calculated from this relation is more accurate than the Cv measured by the calorimeter. In summary, since it is easier to fit the isochoric slop, I was motivated to fit the isochores using isochoric data points of carbon dioxide component. Carbon dioxide data were chosen because it is available in literature, and because carbon dioxide component is one of the important natural gas components that is widely used in industrial applications.

1.6 Objectives of Current Thesis

The main objectives of my thesis are to:

(1) Investigate in using isochoric data points of carbon dioxide component in the development of a simple equation of state.

(2) Use REFPROP (reference fluid and transport properties) software to generate isochoric data points of carbon dioxide and to correct the experimental data.

(3) Use excel, matlab, polymath, to perform regression analysis in order to generate a mathematical model for carbon dioxide using isochoric data.

(4) Prove that isochoric data points of carbon dioxide is able to generated an equation of state obtaining a deviation less than the random error imposed to the data.

(5) As a future work, extend this study into pure components other than carbon dioxide, and into multi-component mixtures.

1. LITERATURE REVIEW

2.1 Cubic Equations of State

Throughout the history, many studies have sought a better representation of the PVT relationship for fluids. The aim of such studies is to increase the accuracy of the thermodynamic properties which is interesting both academically and commercially. As the accuracy of data improves, operational efficiency also improves substantially resulting in significant savings in the cost of chemical plant operations. [34] Equation of state history starts back in 1662 when Boyle found that the volume of gas is inversely proportional to its pressure at a constant temperature. Charles found later that the change in volume is proportional to change in temperature at constant pressure. Clapeyronin 1834 combined the two observations to form the ideal gas law: PV = RT.[35]

The ideal gas law is not an accurate approximation of real gas behavior, because it assumes no interactions among the gas molecules. It also did not consider the finite volume occupied by the molecules. [36] Many attempts have been done to accurately describe the real gas behavior until van der Waals published his famous EOS in 1873. [37] The van der Waals EOS relates pressure, temperature, and molar volume as:

$$P = \frac{R\,T}{V_m - b} - \frac{a}{{V_m}^2} \quad \text{..... (2.1)}$$

In which *a* is the attraction parameter and b is the repulsion parameter (represents the volume occupied by the molecule, also called co-volume). The vdW equation came from describing experimental measurements. However, it can be obtained from statistical mechanics by assuming a hard repulsive potential and an inverse 6^{th} power

attractive potential. [38] The parameters *a* and *b* can be calculated from critical point conditions:

$$\left(\frac{\partial P}{\partial Vm}\right)_{Tc} = 0 \quad \text{(2.2)}$$

$$\left(\frac{\partial^2 P}{\partial Vm^2}\right)_{Tc} = 0 \quad \text{(2.3)}$$

Which produce:

$$a = \frac{27}{64}\frac{R^2(T_c)^2}{P_c} \quad \text{(2.4)}$$

$$b = \frac{R\,T_c}{8\,P_c} \quad \text{(2.5)}$$

Many extensions of the vdW EOS appeared in the last century attempting to increase its accuracy, until Redlich and Kwong[39] proposed their equation in 1949:

$$P = \frac{R\,T}{V_m - b} - \frac{a\,\alpha}{v_m\,(v_m + b)} \quad \text{(2.6)}$$

$$\alpha = \frac{1}{T^{0.5}} \quad \text{(2.7)}$$

By applying the critical point conditions, parameters *a* and *b* can be calculated in terms of the critical properties. The major limitation of the RK EOS is its inability to describe the critical region, thus reducing its accuracy when calculating vapor-liquid equilibria. However, this equation can be improved by introducing more complex temperature dependence to the *a* parameter that also incorporates the acentric factor, ω. Soave[40]proposed this modification in 1972. He showed that the new EOS was a significant improvement over RK for pure hydrocarbons and for hydrocarbon mixtures when calculating VLE. The Soave α parameter provides a good fit to the vapor pressure of hydrocarbon components.

$$P = \frac{R\,T}{V-b} - \frac{a_c\,\alpha\,(T_r,\omega)}{V\,(V+b)} \quad \text{(2.8)}$$

$$a_c = 0.42747\,\frac{R^2 T_c^{2.5}}{P_c} \quad \text{(2.9)}$$

$$b = 0.08664\,\frac{R\,T_c}{P_c} \quad \text{(2.10)}$$

$$\alpha(T_r,\omega) = [\,1 + \left(1 - T_r^{\,0.5}\right)(\,0.480 + 1.574\,\omega - 0.176\omega^2)]^2 \quad \text{(2.11)}$$

The Soave equation received significant attention from academia and industry. After that, the academic community became interested in modifying equations of state, which provide more accurate thermo-physical properties. In 1976, Peng Robinson [41] proposed the currently most popular EOS in industrial applications:

$$P = \frac{R\,T}{V_m - b} - \frac{a\,\alpha(T_r,\omega)}{V_m\,(V_m+b)+b\,(V_m-b)} \quad \text{(2.12)}$$

$$a_c = 0.45724\,\frac{R^2 T_c^{2.5}}{P_c} \quad \text{(2.13)}$$

$$b = 0.07780\,\frac{R\,T_c}{P_c} \quad \text{(2.14)}$$

$$\alpha(T_r,\omega) = [\,1 + \left(1 - T_r^{\,0.5}\right)(\,0.37464 + 1.54226\,\omega - 0.26992\omega^2)]^2 \quad \text{(2.15)}$$

The Peng Robinson equation of state describes the critical region better than most other cubic EOS, and it can calculate the vapor pressure and compositions of hydrocarbon mixtures at equilibrium. However, it is not very accurate when predicting thermal and caloric properties or saturated densities of liquids. The Peng Robinson equation of state was mostly developed to:

- Express the two parameters in terms of Tc, Pc, and ω.
- Make calculations near the critical point accurate enough to provide reasonable results for compressibility factor and liquid density.

- Provide a model that is applicable to all hydrocarbon fluids.
- Include mixing rules among molecules that do not employ more than a single binary interaction parameter and are independent of (T, P, and x).

In general, the PR and SRK equations are used widely to calculate the properties of pure components and mixtures [42]. In addition, they can predict VLE, LLE, and derivatives of thermodynamic properties. However, PR is superior in predicting the liquid densities of many materials, especially non-polar ones.

It should be noted that the four mentioned equations of state are common in having two parameters only. To increase accuracy, some authors have proposed equations using more than two parameters in the equation of state. One of the most popular three-parameter cubic equations of state was proposed by Patel and Teja [43] in 1982:

$$P = \frac{R\,T}{V_m - b} - \frac{a_c\,\alpha(T)}{V_m(V_m + b) + c\,(V_m - b)} \quad \text{(2.16)}$$

In which the three parameters a, b, and c, in addition to α are functions of the reduced pressure and temperature. The generalized PT equation has been successfully applied to correlate VLE in mixtures. [44-47]

Some serious deficiencies exist with respect to the representation of thermal and caloric properties in the liquid phase. Klimeck[48] summarized the weaknesses that are common in cubic equations of state as:

- PR does not provide very accurate description of PρT relation of pure methane. The density calculated by PR deviates from the reference equation of state of Setzmann and Wagner by up to 5 % at pressures below 30 MPa.

- Speed of sound calculations show deviations of more than ± 10% in the same temperature and pressure ranges.
- Saturated liquid densities calculated deviate up to 15% from experimental data for natural gases and state-of-the art measurements on pure substances.
- Compressed liquid densities are inaccurate compared to the experimental measurements.

The data discussed demonstrate that Peng Robinson equation of state does not provide an accurate description of thermal and caloric properties in the homogeneous region and for saturated-liquid densities. However, PR equation is accurate enough in predicting vapor pressures and equilibrium-phase compositions of mixtures. [49]But there is still many ways to make cubic equations of state more accurate in predicting thermal and caloric properties.

2.2 Application to Mixtures

Classical mixing rules can determine the parameters of equations of state applied to multi-component fluid mixtures. Essentially, mixing rules describe the intermolecular forces that exist among the different components molecules. Van der Waals extended his cubic equation of state to mixtures using a simple, one fluid model. He used the same equation of state applied to pure fluids but extended by obtaining new parameters for the mixture. The parameters *a* and *b* presented in the vdW equation need appropriate mixing rules to account for molecular interactions. The simplest forms for the parameters are:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j a_{ij} \quad \text{(2.17)}$$

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j b_{ij} \quad \text{(2.18)}$$

For the Patel and Teja equation of state, parameter *c* has similar mixing rules. These mixing rules are reliable and reasonably accurate. Therefore, other complex mixing rules are not as well-known as this model. Besides mixing rules, binary interaction parameters sometimes improve the accuracy of the equation of state. The SAFT and PC-SAFT molecular-based equations use one binary interaction parameter in the one-fluid model to obtain the mixture parameters. [50-51]

2.3 Non Cubic Equations of State

Beside cubic equations derived from the observation of van der Waals, several equations of state can be based on virial equations or obtained from statistical mechanics and computer simulations.

The virial equation is typically an empirical form; however it has a sound basis in statistical mechanics. It has the forms of power series in density and pressure [52]. Its weakness lies in failing to predict multiple-phase properties. Knowing that, each equation of state can be viable in a specific fluid region in which the calculation of thermodynamic properties is required. A large number of equations of state published in the literature differ in structure and accuracy. Some of the models describe the behavior of the mixture using excess properties. For example, models that express excess Gibbs free energy [53-54] or excess Helmholtz free energy [55-56].According to [Orbey and Sandler][57], these models are not suitable for most engineering problems because pure components and mixtures should be in the same state at the existing temperature and pressure. Some equations of state are explicit in pressure, such as cubic and empirical equations of state.

The Bender and Starling equations are examples of empirical equations. They use mixing rules to describe the composition dependence of the coefficients and the temperature dependent functions of the equation of state. Thus, they improve the description of the properties of mixtures especially in the homogeneous region. Some equations of state deals with liquids only. The SGERG equation of Jaeschke and Humpherys[58] is an example of the equations which deals only with gas phase properties of natural gases, and can be applied for pipeline transportation. These equations use mole fractions of specific natural gas components in combination with physical properties instead of the complete molar composition analysis. It is not an easy task to predict a model that can be applicable for different fluid regions. [59] However, some equations can be applicable to wider range, than others, to cover many regions. AGA8-DC92 equation is an example of standard natural gas applications that are located in the classical natural gas region at temperatures from (250 to 350) K and pressures up to 30 MPa. This equation was internationally accepted standard. GERG-2008 equation is another example of a good models. It is explicit of Helmholtz free energy, and has the potential to cover gas phase, liquid phase, supercritical region, and VLE for natural gas mixtures.

2.3.1. AGA8-DC92 Equation of State

AGA8-DC92 equation of state is very useful model. It was internationally accepted for the calculation of thermodynamic properties according to international standard (ISO). Its range of validity is limited to the gas phase and covers temperatures from(143 to 673) K and pressures up to 280MPa, but it is more accurate in temperature

range of (250 to 350) K and up to 30 MPa. [60] Numerous authors [61-63] have provided detailed investigations of the uncertainty associated with AGA8-DC92 and thermal and caloric properties calculated with it.

The results of the investigation are:

- In the description of the PρT relation of typical natural gases, the uncertainty of density is 0.1% for temperatures ranging from (290 to 350) K at pressures up to 30 MPa. However, uncertainty in the prediction of thermal properties in the temperature ranges from (250 to 270) K is higher.
- The uncertainty of thermal properties increases for natural gases containing small fractions of nitrogen, carbon dioxide, ethane, or heavier hydrocarbons in lower temperature range.
- For caloric properties, significant deviations can be noticed between experimental and calculated data below 270 K. speed of sound for instance deviate increasingly at higher pressures to reach a value of about -1% at a pressure of 20 MPa. Moreover, above 270 K the uncertainty in speed of sound amounts to approximately 0.2 %. Whereas, in isobaric heat capacity and isobaric enthalpy uncertainty is about 1 %.
- For natural gases containing higher fractions of heavier hydrocarbons such as propane and the butanes, the uncertainty in caloric properties increase.

2.3.2. GERG-2008 Equation of State

The GERG-2008 equation of state is an expansion of GERG-2004 used for natural gases and other mixtures developed by Kunz [64]. This equation is explicit in the

Helmholtz energy which is a function of density, temperature, and composition. GERG-2008 covers 21 natural gas components, and it is adequate over wide ranges of pressure, temperature, and composition. It has the potential to cover gas phase, liquid phase, supercritical region, and VLE for natural gas mixtures. What makes this equation special is its updated database which contains more than 125,000 experimental data points for multiple thermodynamic properties. Of the experimental data, ¾ accounts for binary mixtures, and the rest accounts for multi-component mixtures.

Because the GERG-2008 model is a multi-fluid approximation and explicit in the Helmholtz free energy, the real Helmholtz function is divided into an ideal gas mixture part and the residual mixture part:

$$\alpha(\delta,\tau,x) = \alpha^0(\rho,T,x) + \alpha^r(\delta,\tau,x) \quad \text{(2.19)}$$

Where δ is the reduced density for mixtures, and τ is the inversely reduced temperature for mixtures:

$$\tau = {}^{T_r}/_{T} \quad \text{(2.20)}$$

$$\delta = {}^{\rho}/_{\rho_r} \quad \text{(2.21)}$$

Where T_r and ρ_r are dependent of composition. For the ideal gas mixture$\alpha^0(\rho,T,x)$, the dimensionless form of the Helmholtz free energy is given by:

$$\alpha^0(\rho,T,x) = \sum_{i=1}^{N} xi\,[\alpha_i{}^0(\rho,T) + \ln xi] \quad \text{(2.22)}$$

Where N = the number of components in the mixture,

$\alpha_i{}^0(\rho,T)$ = Helmholtz free energy (Ideal gas state)

xi = mole fraction of the mixture components

$xi \ln xi$ Account for the entropy of mixing

Whereas, the residual part of the reduced Helmholtz free energy $\alpha^r(\delta, \tau, x)$ is given by:

$$\alpha^r(\delta, \tau, x) = \sum_{i=1}^{N} xi\ \alpha_i{}^r(\delta, \tau) + \Delta\alpha^r(\delta, \tau, x) \quad \ldots\ldots\ldots\

hydrocarbon mixtures and satisfies the demand on the accuracy in the description of vapor-liquid equilibrium. The GERG-2008 equation can be viable in natural gas pipeline transport, storage, liquefaction, production and in natural gas separation processes.

3. RESEARCH PROCEDURE

In my research project, I investigated the use of isochoric data in the development of a simple EOS for carbon dioxide. I had four main steps in my thesis. As shown in figure (3.1), the first step was to use REFPROP (reference fluid and transport properties) program to generate the isochoric data points for carbon dioxide and to correct the experimental data in order to get true isochore. The experimental data are relatively sparse in literature. However, I had to use the limited experimental data obtained by our team in college station. [65]. REFPROP is a powerful database program available from NIST[66]. It is able to calculate the thermodynamic and transport properties for pure fluids and their mixtures using the most accurate models available.

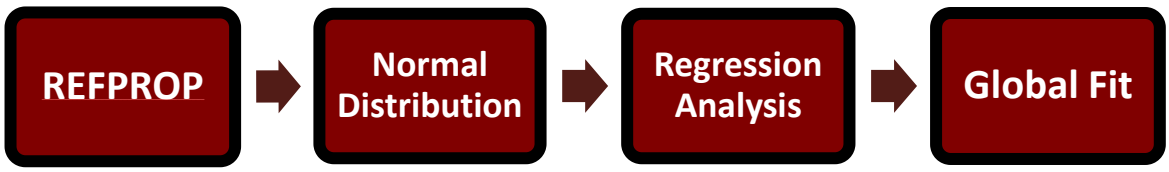


Figure (3.1): The main four steps in the master thesis research

The second step was to impose random error to the generated data to get generated pressure and temperature using normal distribution. Gaussian equation was used in the normal distribution method and 2 sigma region was chosen in the generated data I obtained.

The third step was to perform regression analysis in the eight models I developed. I performed regression analysis twice, the first timeI worked with the derivative of *P* (and P - P saturation) with respect to *T*(and 1/T, 1/T – 1/T saturation, 1/T-T saturation, T –T saturation)to determine the dependence of pressure upon temperature. Then, I determined the dependence of the coefficients of the first equation upon volume (density). This operation gave me an equation for pressure in terms of temperature and volume or density.

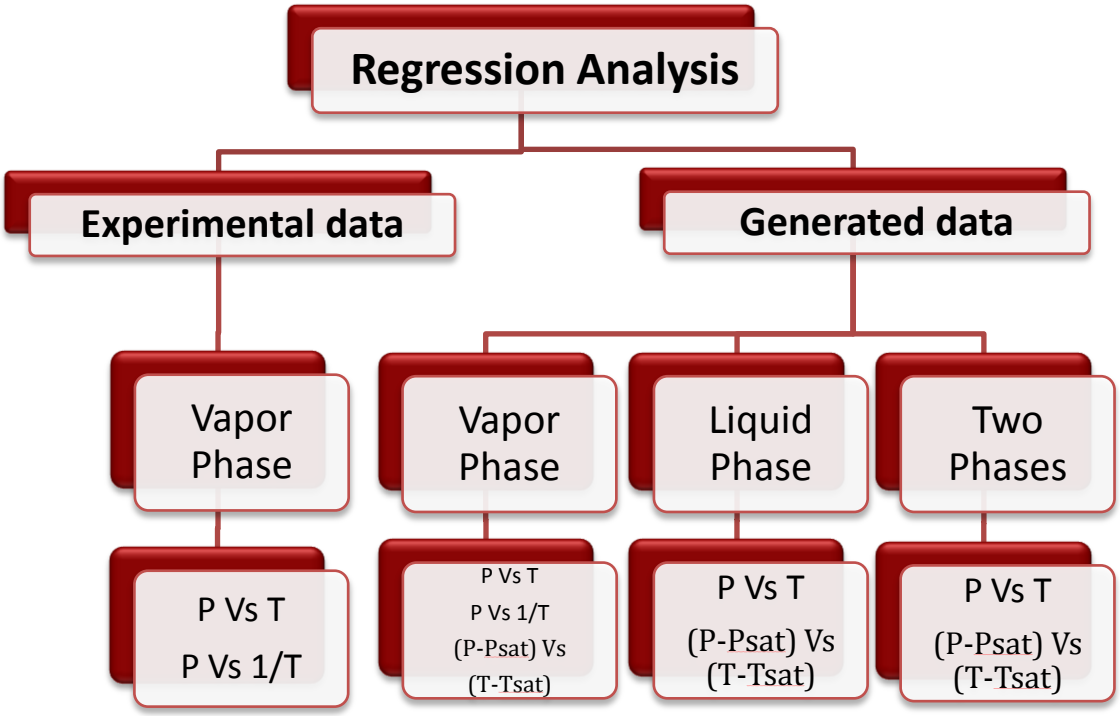


Figure (3.2): The nine studies performed in the master thesis research

Figure (3.2) above shows the nine studies I performed on the experimental and generated data. Among the nine models I developed, two models used the experimental data and the rest used the generated data. There has been more focus on the vapor phase in my thesis, and that is because the models I developed had a virial type equation of state which is more accurate in the vapor phase of carbon dioxide.

Regression analysis was used to determine the structure of the model proposed in both steps. Regression modeling is one of the most widely used statistical modeling techniques to fit a quantitative variable of pressure as a function of one or more predictor variables, as temperature and density in my case. There are several types of regression models being able to describe a mathematical relationship, however, I used linear least squares regression analysis in estimating the model parameters[67-68].The nine models I developed had linear relationship in terms of the parameters.

The fourth step was to perform a global fit using Polymath 6.1 program to determine the coefficients and to calculate the deviation between predicted and experimental data. By the global fit step, I could plot the residual (P calculated – P generated) and the deviation (% error) between the model developed and the data I started with in my study. If the developed model obtains a deviation less than the random (or experimental) error, this means the model developed is quite reliable and accurate in predicting the physical properties. But, the aim of this thesis is still not to develop high accurate equation of state for carbon dioxide component. The aim was to show a technique of generating an equation of state using isochoric data points. This procedure should establish the efficacy of using isochoric data for EOS development

4. RESEARCH RESULTS

In this chapter, I will show in more details the steps I did to develop the model proposed in the previous chapter. However, not all the detailed steps will be presented in my thesis. I will present the final outcomes I obtained in this chapter, in addition to some more details in the appendix.

4.1 Experimental Data

Burnett isochoric apparatus was used to generate the isochoric density data in the lab. The experiments consisted of a series of 10 isochores having around eight data points for temperature and pressure at each density [65]. The data obtained were all in the vapor phase of carbon dioxide (Figure 4.1). As was mentioned in the previous chapter, REFPROP was used to correct the pressure obtained experimentally using equation (4.1). Since it is impossible experimentally to maintain constant volume of the isochoric cell, due to the slight expansion and compression of the cell during operation. The pressure obtained needs to be corrected in order to get true isochore. To correct the experimental pressure using REFPROP, the equation below was used to find P*:

$$(P - P^*) = (\rho - \rho^*)\left(\frac{dP}{d\rho}\right)_T \quad (4.1)$$

- P* is the corrected pressure,
- ρ* is the first density measured by the isochoric apparatus.
- P and ρ are the experimental pressure and density respectively.
- $\left(\frac{dP}{d\rho}\right)_T$ Was obtained by REFPROP.

The isochores being used to develop the model, have started from saturated pressure and temperature as figure (4.1) shows. Thus, not all the isochores were used, because some of them had very low density. Six isochores were used in the experimental data to study the dependence of P upon T and P upon 1/T.

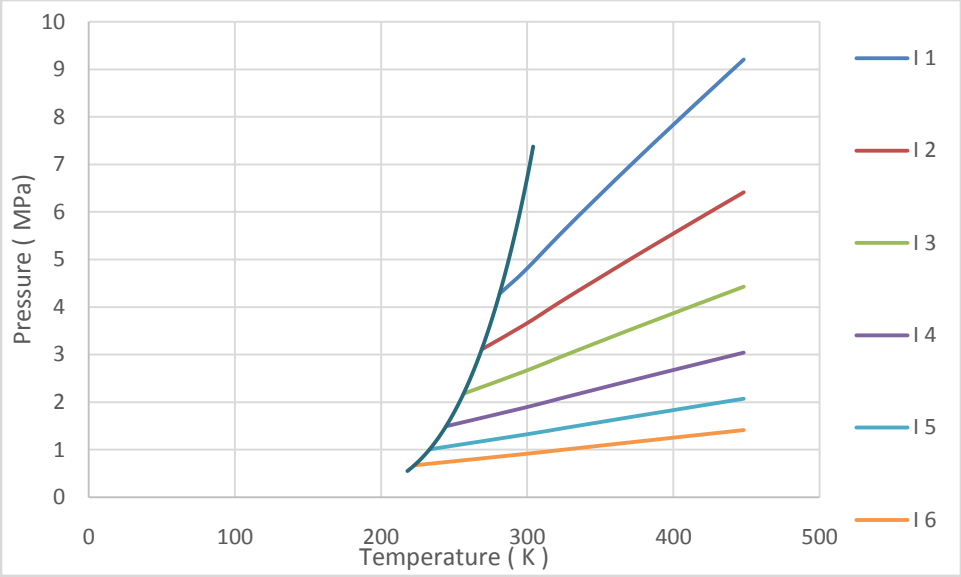


Figure (4.1): Vapor liquid equilibrium with the isochores used in this study of CO_2 (Exp. Data)

4.1.1 Pressure Versus Temperature

I started the modeling by plotting the pressure versus temperature, and obtained the model which best fitted the experimental data. To get the best fit of my data, I performed standard deviation technique using the following equation:

$$\text{Standard Deviation} = \sqrt{\frac{\sum(Pexp - Pcal)^2}{n-2}} \quad \ldots\ldots\ldots\

$$P = a1T + a2T^2 + a3T^3 \quad \text{(4.3)}$$

Polymath 6.1 program was used after that to confirm the results obtained, and to study the relation between the coefficients of the first model and the density. Figures (4.2) to (4.4) show the dependence of the coefficients (a1, a2, and a3) of model (4.3) upon density. For figures (4.2) to (4.4), it can be noticed that the curves start from the origin and each curve has six data points of the ai and the density.

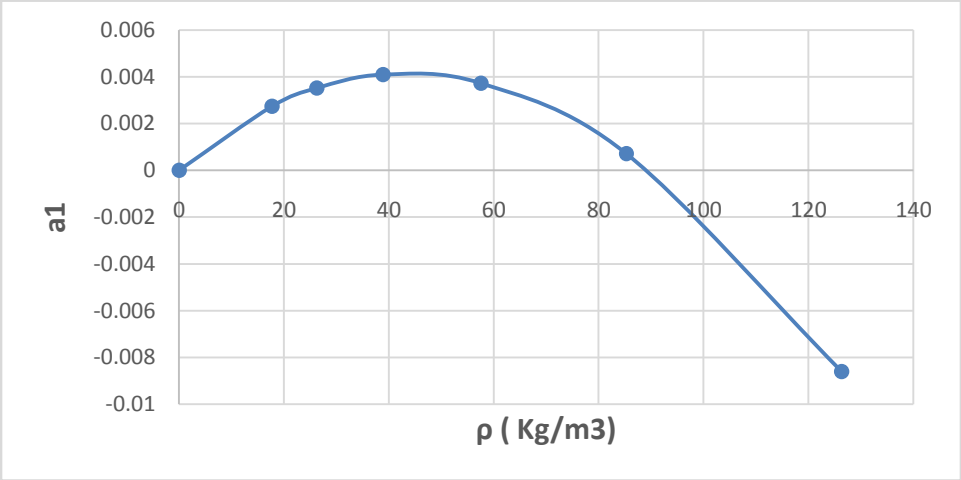


Figure (4.2): The relation between a1 and density for P vs T study of vapor phase (Exp. Data)

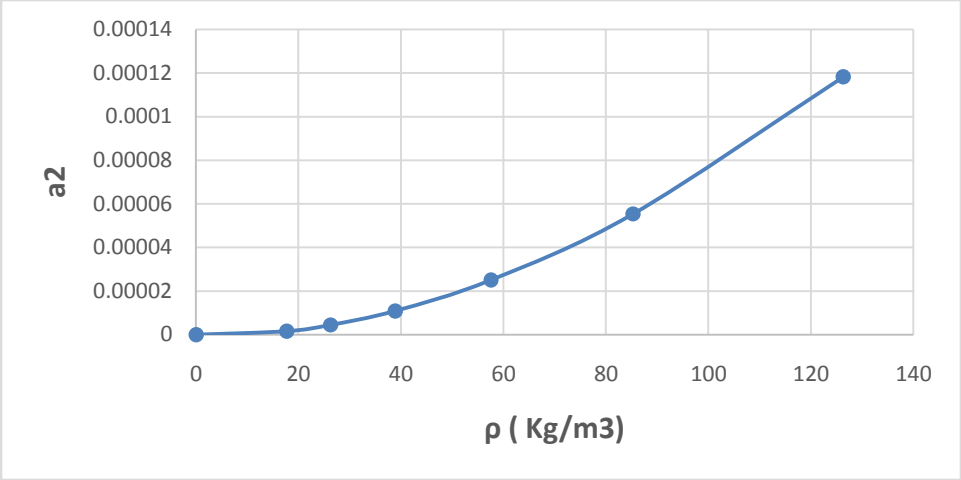


Figure (4.3): The relation between a2 and density for P vs T study of vapor phase (Exp. Data)

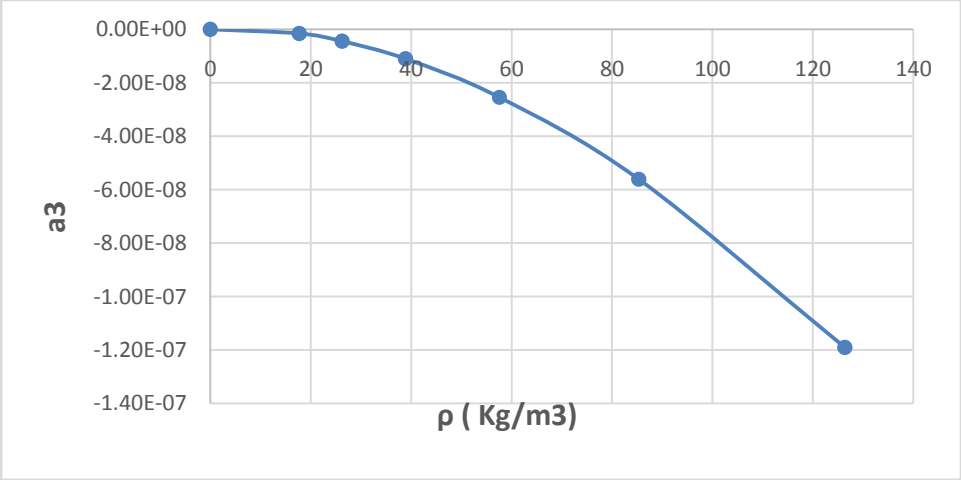


Figure (4.4): The relation between a3 and density for P vs T study of vapor phase (Exp. Data)

In the next step, I studied the relation between the coefficients and the density by fitting each of the three curves. According to the values of the coefficients as well as the variance, the sixth model equation had the least variance and all its coefficients were

significant for the PT relation. Other models were eliminated due to having some insignificant coefficients and/or big comparable variance. The dependence of the coefficients of (4.3) equation upon density came up with the following expression:

$$ai = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 + c6\rho^6 \quad (4.4)$$

After substituting equation (4.4) into equation (4.3), we will get an equation of state expressed in pressure and function of temperature and density of PT relation of the experimental data:

$$P = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5 + c16\rho^6)\,T + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5 + c26\rho^6)T^2 + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5 + c36\rho^6)T^3 \quad (4.5)$$

Polymath was used again to perform global fit analysis. We had 18 model variables in this global fit, and 48 data points of pressure, temperature and density. Figures (4.5) and (4.6) below show the residual and the percentage error obtained in this study respectively. And table (4.1) shows the values obtained for the coefficients of model (4.5).

Table (4.1): Coefficients obtained for P vs T study of vapor phase for the experimental data

Variable	Initial guess	Value	95% confidence
c11	0.0002021	0.000202	0.0006168
c12	-3.00E-06	-2.99E-06	7.14E-05
c13	2.27E-08	2.25E-08	2.96E-06

Table (4.1): Continued.

Variable	Initial guess	Value	95% confidence
c14	-3.41E-10	-3.36E-10	5.54E-08
c15	2.76E-12	2.72E-12	4.70E-10
c16	-8.40E-15	-8.29E-15	1.46E-12
c21	-1.07E-07	-9.87E-08	3.50E-06
c22	1.33E-08	1.23E-08	4.05E-07
c23	-1.59E-10	-1.13E-10	1.68E-08
c24	2.60E-12	1.71E-12	3.14E-10
c25	-2.14E-14	-1.38E-14	2.66E-12
c26	6.54E-17	4.16E-17	8.26E-15
c31	1.28E-10	1.15E-10	4.88E-09
c32	-1.52E-11	-1.34E-11	5.64E-10
c33	2.25E-13	1.40E-13	2.34E-11
c34	-3.88E-15	-2.13E-15	4.36E-13
c35	3.29E-17	1.70E-17	3.70E-15
c36	-1.03E-19	-5.11E-20	1.15E-17

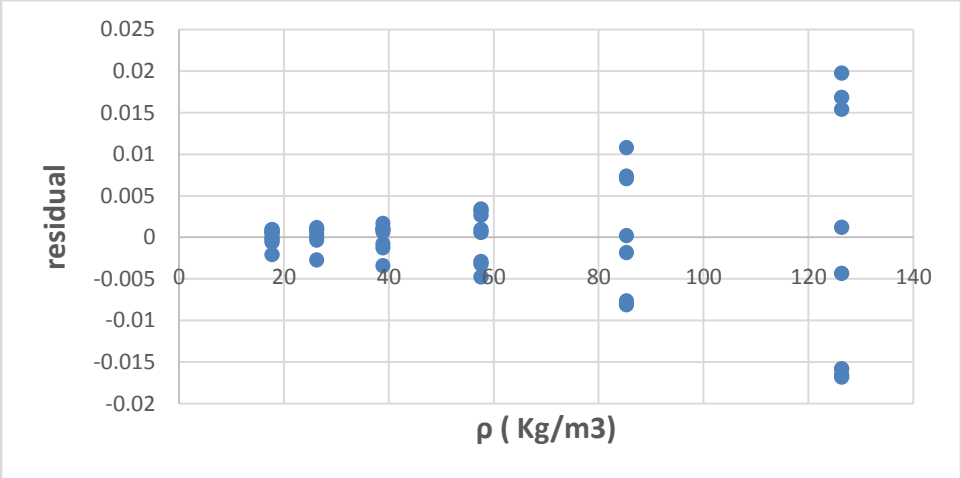


Figure (4.5): Global fit residual for P vs T study of vapor phase (Exp. Data)

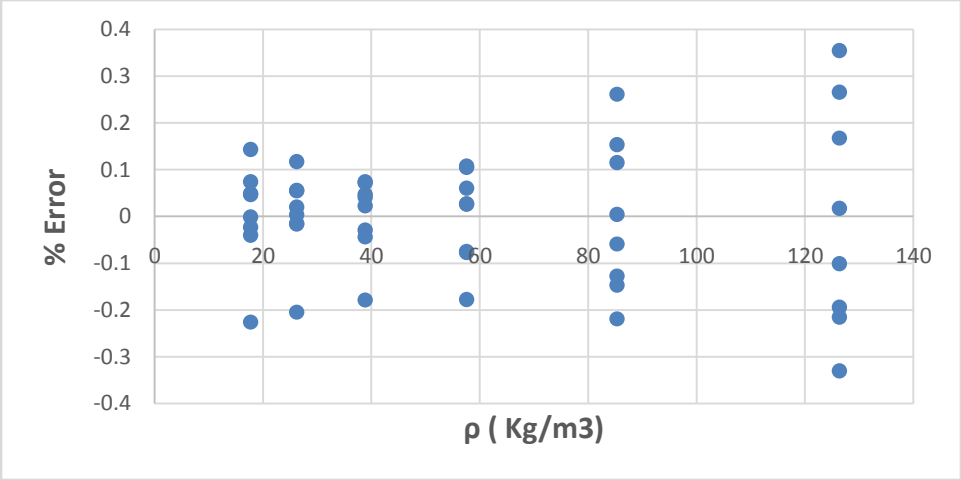


Figure (4.6): Global fit percentage error for P vs T study of vapor phase (Exp. Data)

Figure (4.5) shows very reasonable plot. As the density increase, the residual (P calculated – P generated) increase. According to figure (4.6), the percentage error obtained of this model was ± 0.4. However, the 95% confidence of the results has an error which doesn't exceed ± 0.1. That means this model obtains a deviation within the experimental uncertainty.

4.1.2 Pressure Versus 1/Temperature

In the second study, the relationship between P and 1/T was performed. Since 1/T is considered as a variable in statistical thermodynamics, it is important to include this variable in our studies. P versus 1/T plots obtained different outcomes than P versus T. The least standard deviation of this step was achieved by the quantic model which had the following form:

$$P = b1\frac{1}{T} + b2\frac{1}{T^2} + b3\frac{1}{T^3} + b4\frac{1}{T^4} + b5\frac{1}{T^5} \quad \text{(4.6)}$$

Polymath 6.1 program was used to confirm the results obtained, and to study the relation between the coefficients and the density. Figures (4.7) to (4.11) show the dependence of the coefficients of model (4.6) upon density:

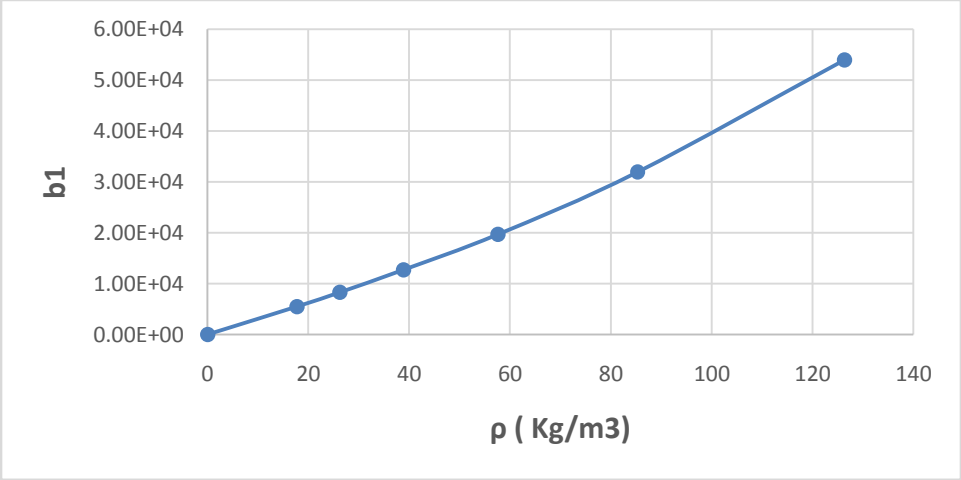


Figure (4.7): The relation between b1 and density for P vs1/T study of vapor phase (Exp. Data)

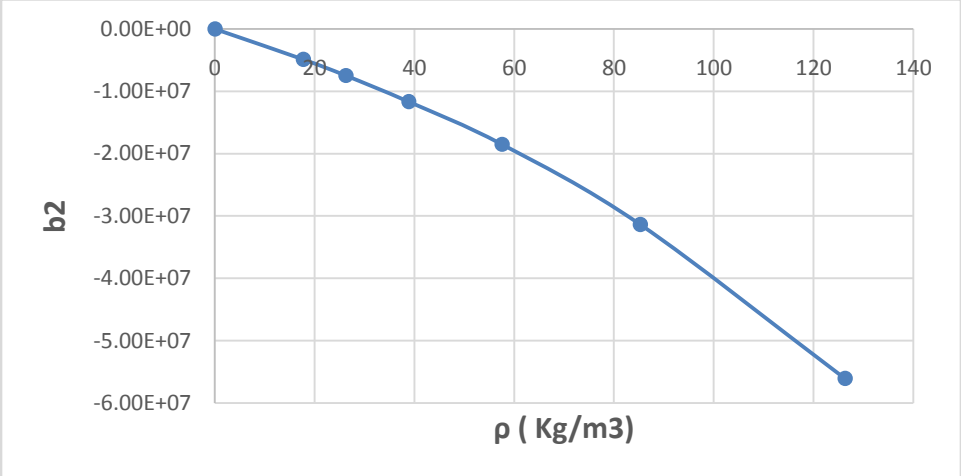


Figure (4.8): The relation between b2 and density for P vs1/T study of vapor phase (Exp. Data)

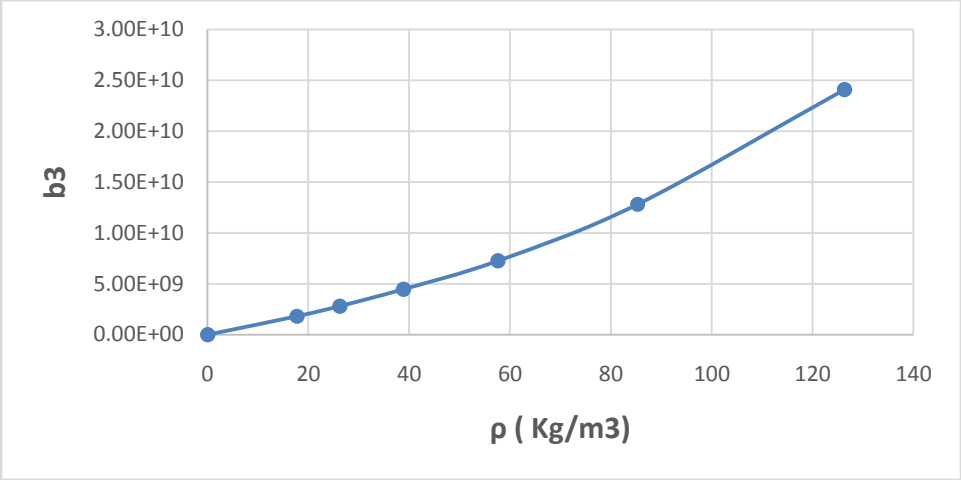


Figure (4.9): The relation between b3 and density for P vs1/T study of vapor phase (Exp. Data)

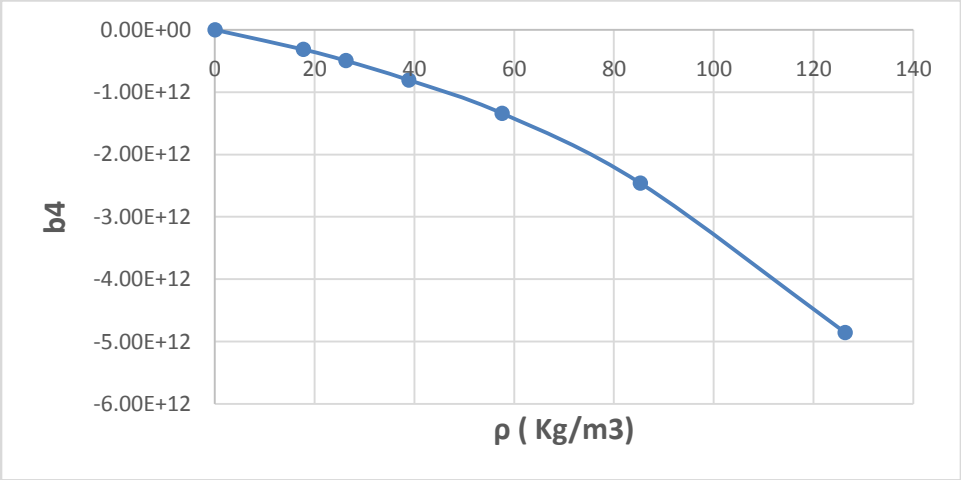


Figure (4.10): The relation between b4 and density for P vs1/T study of vapor phase (Exp. Data)

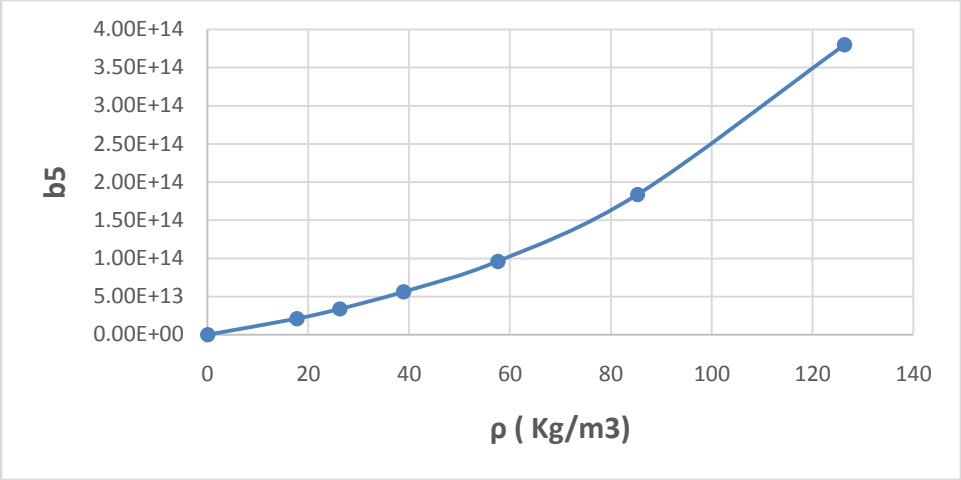


Figure (4.11): The relation between b5 and density for P vs1/T study of vapor phase (Exp. Data)

According to the values of the coefficients and the variance, the sixth model equation had the least variance and all its coefficients were significant for this step. The dependence of the coefficients (bi) of equation (4.6) upon density came up with the following expression:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 + c6\rho^6 \quad \text{(4.7)}$$

After that, equation (4.7) was substituted into equation (4.6)to get an equation of state expressed in pressure and function of temperature and density of P vs 1/T relation:

$$P = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5 + c16\rho^6)\frac{1}{T} + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5 + c26\rho^6)\frac{1}{T^2} + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5 + c36\rho^6)\frac{1}{T^3} + (c41\rho + c42\rho^2 + c43\rho^3 + c44\rho^4 + c45\rho^5 + c46\rho^6)\frac{1}{T^4} + (c51\rho + c52\rho^2 + c53\rho^3 + c54\rho^4 + c55\rho^5 + c56\rho^6)\frac{1}{T^5} \quad \text{(4.8)}$$

Polymath was used again to perform global fit analysis. We had 30 model variables in this global fit, and 48 data points of pressure, temperature and density. Figures (4.12) and (4.13) below show the residual and the error obtained respectively. And table (4.2) show the values obtained for the coefficients of model (4.8).

Table (4.2): Coefficients obtained of Pvs1/T study of vapor phase for the experimental data

Variable	Initial guess	Value	95% confidence
a11	312.8727	317.5693	177.8617
a12	-1.414733	-2.05675	9.08648
a13	0.0995439	0.1307973	0.1993393
a14	-0.0020237	-0.0026924	0.0029337
a15	1.88E-05	2.51E-05	2.50E-05
a16	-6.20E-08	-8.30E-08	8.69E-08
a21	-2.93E+05	-2.84E+05	2.29E+05
a22	3804.025	2572.771	1.10E+04
a23	-228.9585	-170.7897	196.9485
a24	4.725394	3.531858	2.250916
a25	-0.0438143	-0.0330095	0.0193334
a26	0.0001447	0.0001096	7.95E-05
a31	1.02E+08	1.05E+08	1.10E+08
a32	-8.30E+05	-1.18E+06	5.14E+06
a33	6.76E+04	8.20E+04	8.50E+04
a34	-1443.633	-1703.843	744.0098
a35	13.86976	16.00735	6.32529
a36	-0.0468471	-0.05331	0.0328762
a41	-1.84E+10	-1.82E+10	2.29E+10
a42	2.56E+08	2.32E+08	1.09E+09
a43	-1.79E+07	-1.71E+07	2.00E+07
a44	3.70E+05	3.58E+05	2.28E+05
a45	-3464.688	-3386.32	1961.795
a46	11.51362	11.31294	8.623355
a51	1.19E+12	1.19E+12	1.76E+12

Table (4.2): Continued

Variable	Initial guess	Value	95% confidence
a52	-1.51E+10	-1.62E+10	8.67E+10
a53	1.26E+09	1.31E+09	1.93E+09
a54	-2.68E+07	-2.77E+07	2.87E+07
a55	2.57E+05	2.64E+05	2.53E+05
a56	-865.9316	-884.3051	959.0498

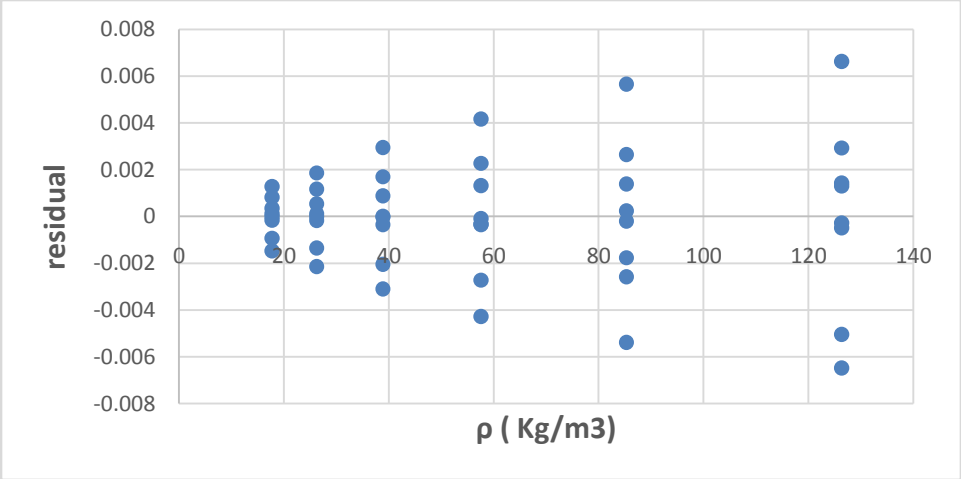


Figure (4.12): Global fit residual for P vs 1/T study of vapor phase (Exp. Data)

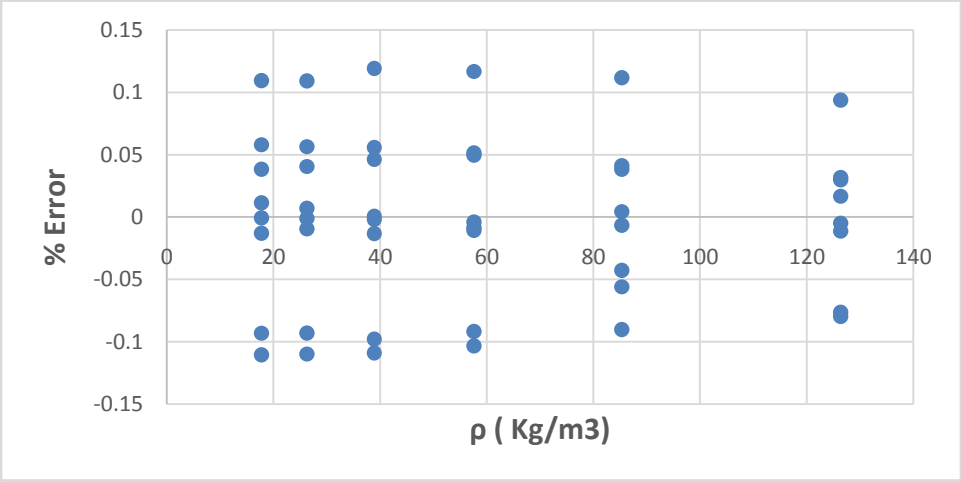


Figure (4.13): Global fit percentage error for P vs 1/T study of vapor phase (Exp. Data)

According to figure (4.13), the percentage error obtained of this model was ± 0.15. However, the 95% confidence of the results has an error which doesn't exceed ± 0.05. That means this model obtains a deviation less than the experimental uncertainty. This model has less deviation than P Versus T model. That means P Versus 1/T study obtains less deviation than P Versus T study.

4.2 Generated Data

Using REFPROP, I obtained data of pressure and temperature for carbon dioxide in liquid and vapor phases. The isochores ranged from 100 Kg/m^3 to 1000 Kg/m^3. The isochores temperature was up to 400 K, and pressure was up to 10 MPa and 100 MPa for vapor and liquid phases respectively. The figure below shows the 13thisochors will be used in the next seven studies of my project.

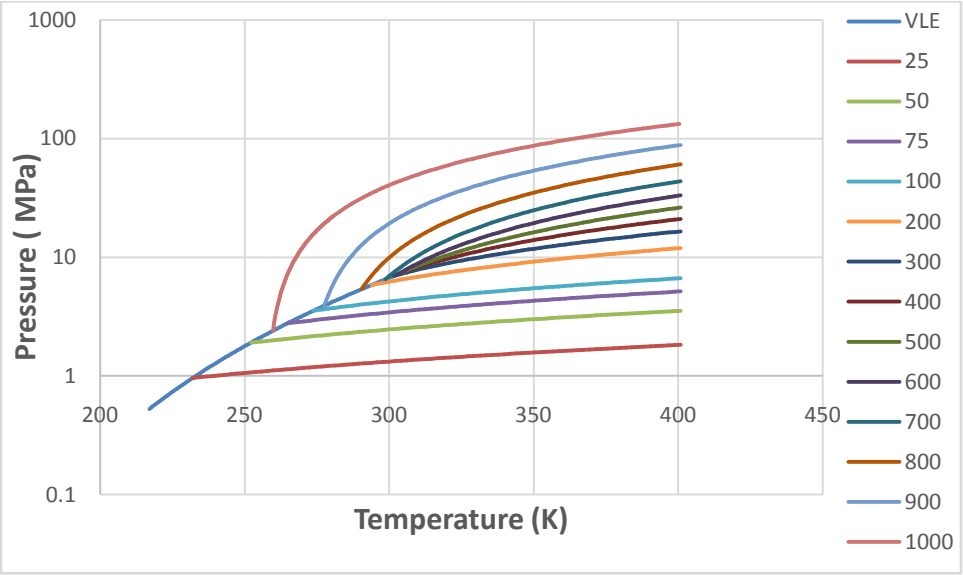


Figure (4.14): The vapor liquid equilibrium with the isochors used in this study of CO_2 (Gen. Data)

I introduced random errors into these pseudo-data using data analysis in excel program. In this case we firstly had data generated by REFPROP, and imposed random error to the data by excel. Gaussian distribution equation was used to impose the random error, and 2 sigma region was used to cover 95% of the data in my studies. Generated temperature and pressure were calculated by the following method:

T generated = n + T experimental……...……..……...…… (4.9)

P generated = (1+n) * P experimental…….……..…….. (4.10)

Where n is the random number generated. In Gaussian distribution method, the mean was zero and the standard deviation was 0.001 MPa or 0.01 MPa for pressure and 10 mK for temperature. The reason for that is because we assumed that pressure transducer was used in the Burnett apparatus, which has uncertainty of 0.01%. To get sigma value, we divide the uncertainty by 100 and multiply by the highest scale of pressure, as shown below. The highest scale in the vapor phase was 10 MPa and for the liquid phase was 100 MPa. Whereas, the uncertainty of temperature is always ± 10mK.

0.01% * 1/100 = 0.0001 * 10 = 0.001 for vapor phase

0.01% * 1/100 = 0.0001 * 100 = 0.01 for liquid phase

The random error for temperature is 10 mk and for pressure is 0.1%mpa for vapor phase and 1% for the liquid phase.

0.01% * 10 = 0.1% for vapor phase

0.01% * 100 = 1% for liquid phase

4.2.1 Vapor Phase Study

I started this part of my thesis by developing two equations to describe the vapor and liquid phases separately. The first equation considered the vapor phase isochores only. I developed two models covering the vapor phase. Both equations were expressed in pressure, but the first one as function of T and the second one as function of 1/T. Seven isochores were used in this step.

I followed the same procedure described before, and used the fifth power equation this time, which showed the best fit. The fifth power equation had the following form:

$$P = b1T + b2T^2 + b3T^3 + b4T^4 + b5T^5 \quad (4.11)$$

After that, I used polymath to obtain the second equation which takes care of the relation between the coefficients and density. Figures (4.14) to (4.18) show the relation between the coefficients and the density. From the figures below, we can notice that there are eight data points in the curves. That is because I included seven isochores in this study in addition to the origin point which make a total of eight data.

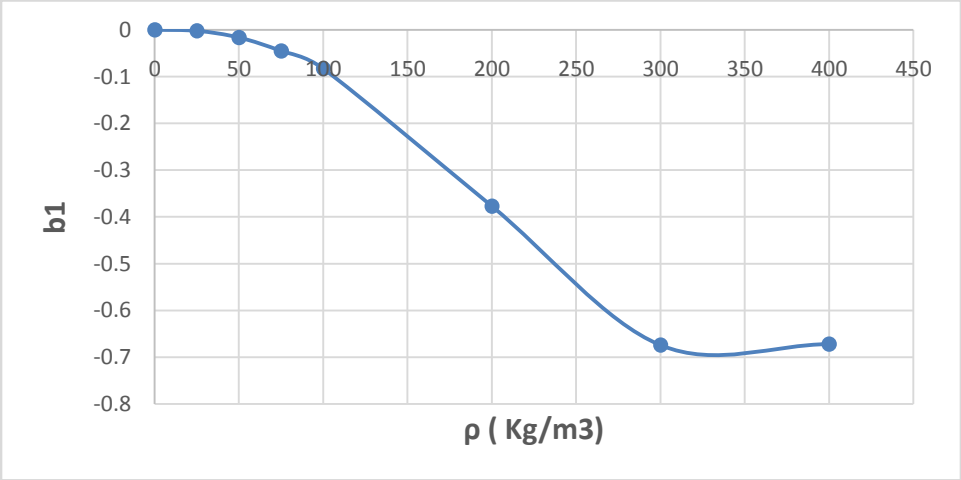


Figure (4.15): The relation between b1 and density for P vs T study of vapor phase (Gen. Data)

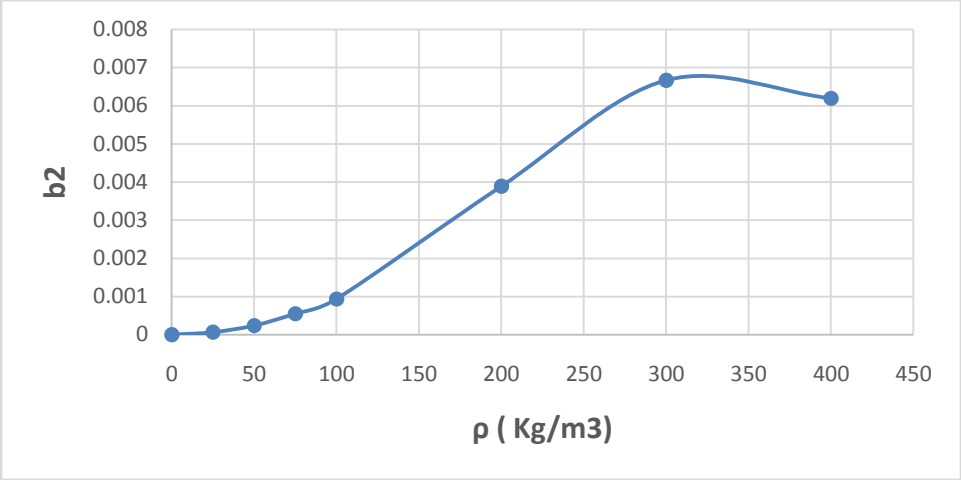


Figure (4.16): The relation between b2 and density for P vs T study of vapor phase (Gen. Data)

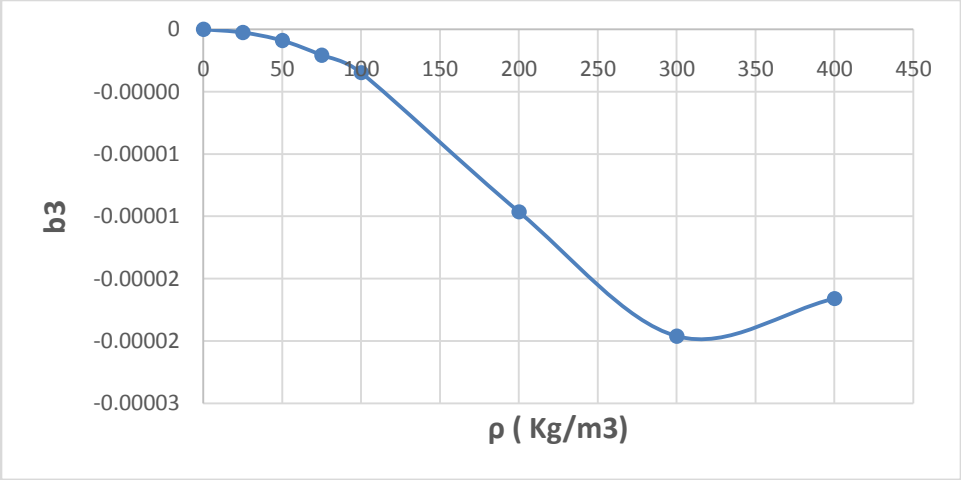


Figure (4.17): The relation between b3 and density for P vs T study of vapor phase (Gen. Data)

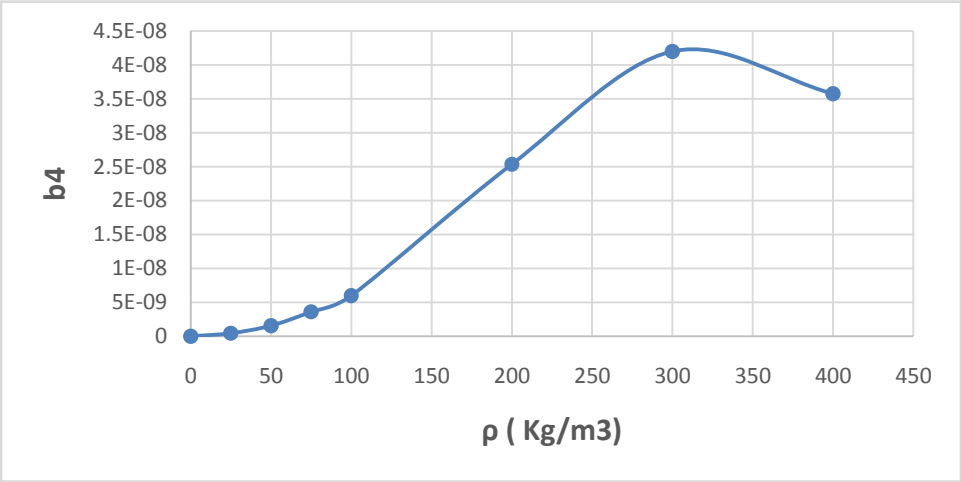


Figure (4.18): The relation between b4 and density for P vs T study of vapor phase (Gen. Data)

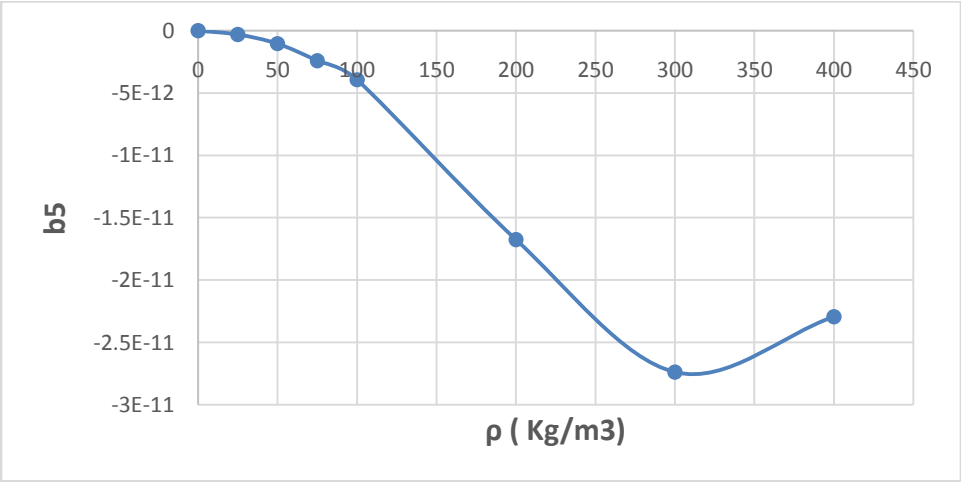


Figure (4.19): The relation between b5 and density for P vs T study of vapor phase (Gen. Data)

After that, I obtained the best model to fit the relation between the coefficients and the density. It was seventh order model, and had the following form:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 + c6\rho^6 + c7\rho^7 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.12)$$

After substituting equation (4.12) into equation (4.11), we will get an equation of state expressed in pressure and function of temperature and density of P vs T relation in the vapor phase:

$$P = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5 + c16\rho^6 + c17\rho^7)\,T + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5 + c26\rho^6 + c27\rho^7)T^2 + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5 + c36\rho^6 + c37\rho^7)T^3 + (c41\rho + c42\rho^2 + c43\rho^3 + c44\rho^4 + c45\rho^5 + c46\rho^6 + c47\rho^7)T^4 + (c51\rho + c52\rho^2 + c53\rho^3 + c54\rho^4 + c55\rho^5 + c56\rho^6 + c57\rho^7)T^5 \quad \ldots\ldots\ldots\

Table (4.3): Continued.

Variable	Initial guess	Value	95% confidence
a24	-9.37E-11	-9.10E-11	5.97E-12
a25	5.26E-13	5.11E-13	1.17E-14
a26	-1.36E-15	-1.32E-15	2.32E-17
a27	1.29E-18	1.25E-18	3.00E-20
a31	-1.81E-08	-1.82E-08	1.42E-08
a32	9.58E-10	9.67E-10	5.33E-10
a33	-3.45E-11	-3.48E-11	5.73E-12
a34	4.08E-13	4.11E-13	2.06E-14
a35	-2.29E-15	-2.31E-15	2.01E-17
a36	5.92E-18	5.97E-18	1.01E-19
a37	-5.61E-21	-5.66E-21	1.36E-22
a41	3.64E-11	3.63E-11	2.88E-11
a42	-2.02E-12	-2.02E-12	1.04E-12
a43	6.94E-14	6.92E-14	1.04E-14
a44	-8.23E-16	-8.20E-16	2.95E-17
a45	4.63E-18	4.61E-18	1.04E-19
a46	-1.20E-20	-1.19E-20	4.28E-22
a47	1.14E-23	1.13E-23	4.65E-25
a51	-2.75E-14	-2.71E-14	2.18E-14
a52	1.58E-15	1.54E-15	7.64E-16
a53	-5.26E-17	-5.14E-17	7.11E-18
a54	6.26E-19	6.10E-19	2.30E-20
a55	-3.52E-21	-3.43E-21	1.66E-22
a56	9.10E-24	8.86E-24	5.40E-25
a57	-8.63E-27	-8.39E-27	5.46E-28

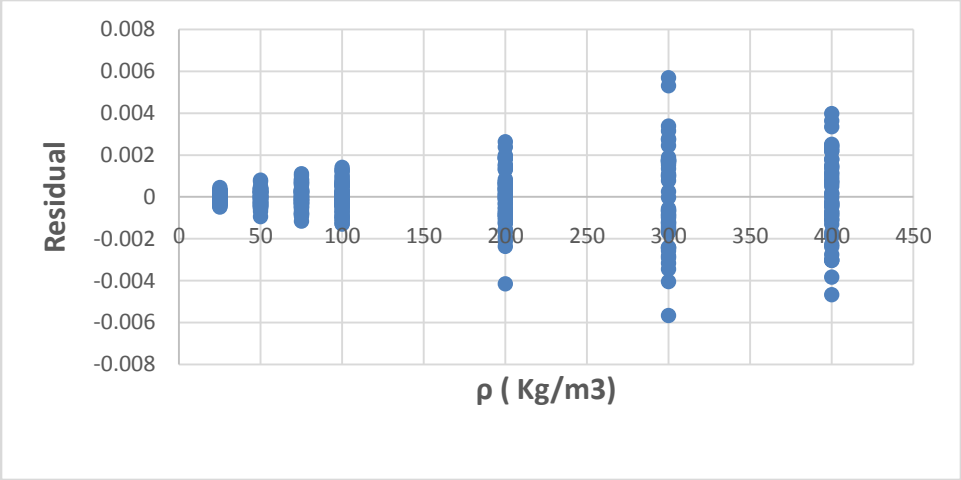


Figure (4.20): Global fit residual for P vs T study of vapor phase (Gen. Data)

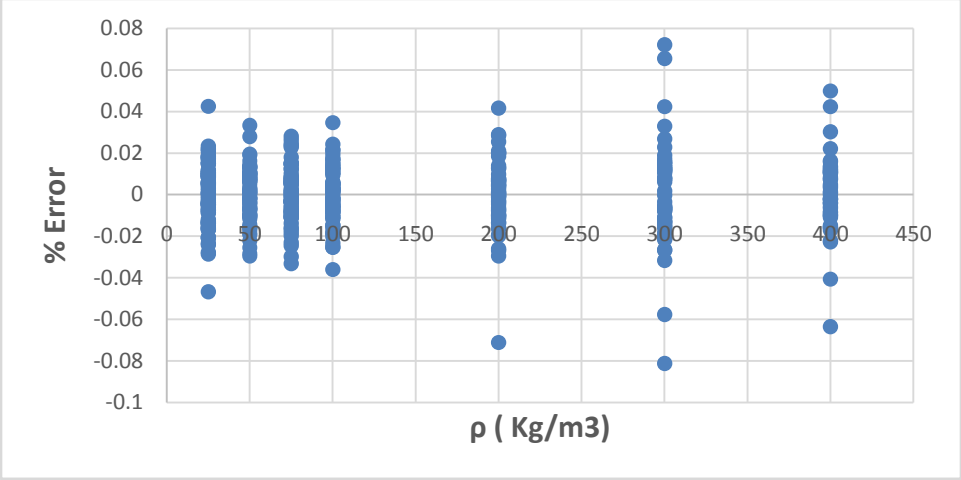


Figure (4.21): Global fit percentage error for P vs T study of vapor phase (Gen. Data)

According to figure (4.21), the percentage error obtained of this model was ± 0.1. However, the 95% confidence of the results has an error which doesn't exceed ± 0.04.

That means this model obtains a deviation less than the random error imposed to the data, which is 0.1%.

The second model of vapor phase studied the dependence of pressure upon 1/temperature. The sixth power model had the best fit in this study, having the following form:

$$P = b1\frac{1}{T} + b2\frac{1}{T^2} + b3\frac{1}{T^3} + b4\frac{1}{T^4} + b5\frac{1}{T^5} + b6\frac{1}{T^6} \quad \text{..... (4.14)}$$

After that, I plotted the relation between the coefficients and density to obtain the second model. Figures (4.22) to (4.27) show the relation between the coefficients and density. It can be noted in figure (4.27) that b6 has only 5 isochoric data points. The first point is the origin, and the rest are the first four isochores which had random residual among the seven isochores. The rest of the isochores had systematic residual which is unacceptable in statistical techniques. The coefficients b1 to b5 had eight isochoric data points, but only b6 had four data.

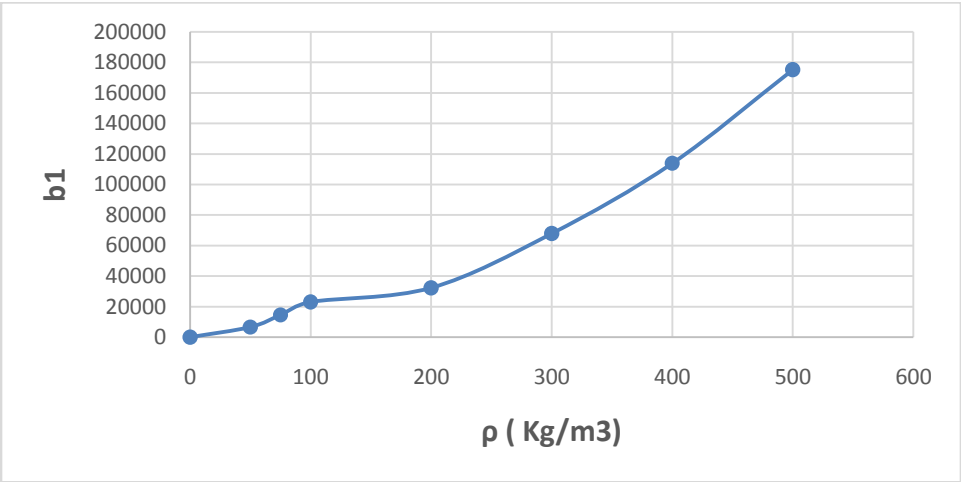


Figure (4.22): The relation between b1 and density for Pvs1/T study of vapor phase (Gen. Data)

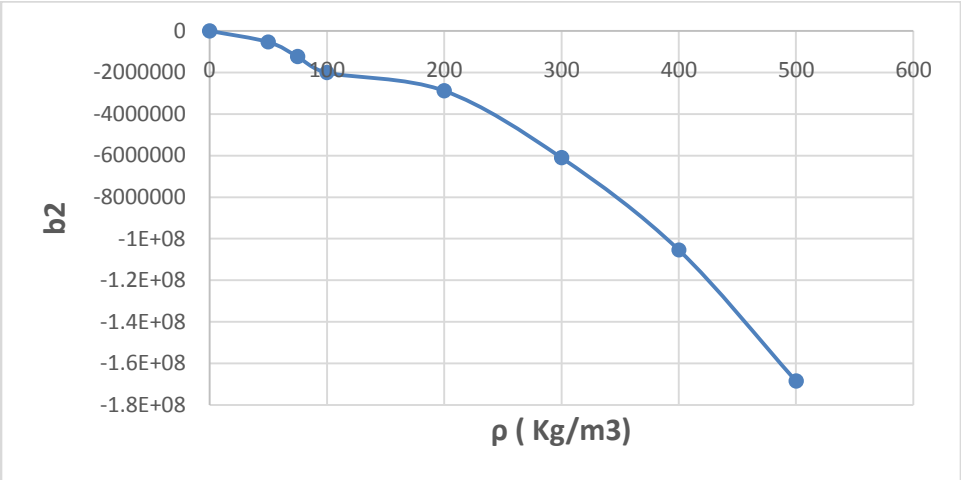


Figure (4.23): The relation between b2 and density for P vs1/T study of vapor phase (Gen. Data)

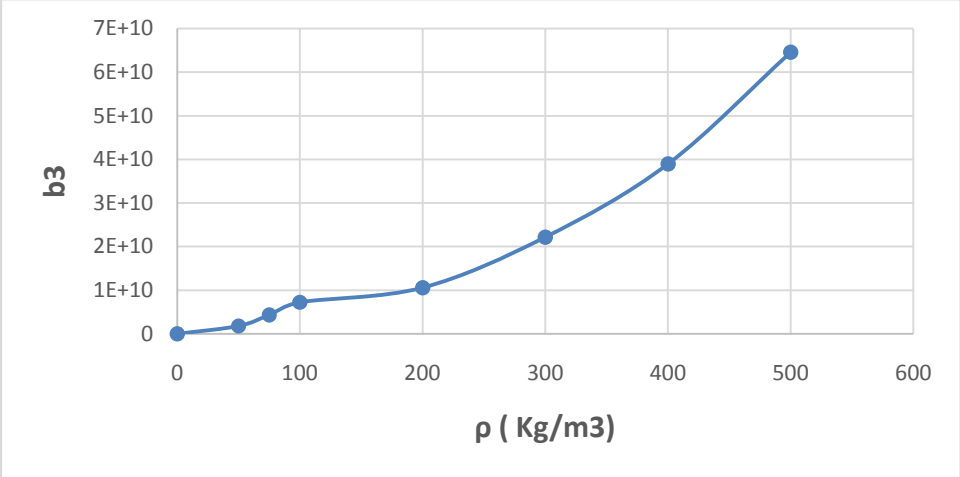


Figure (4.24): The relation between b3 and density for P vs1/T of vapor phase (Gen. Data)

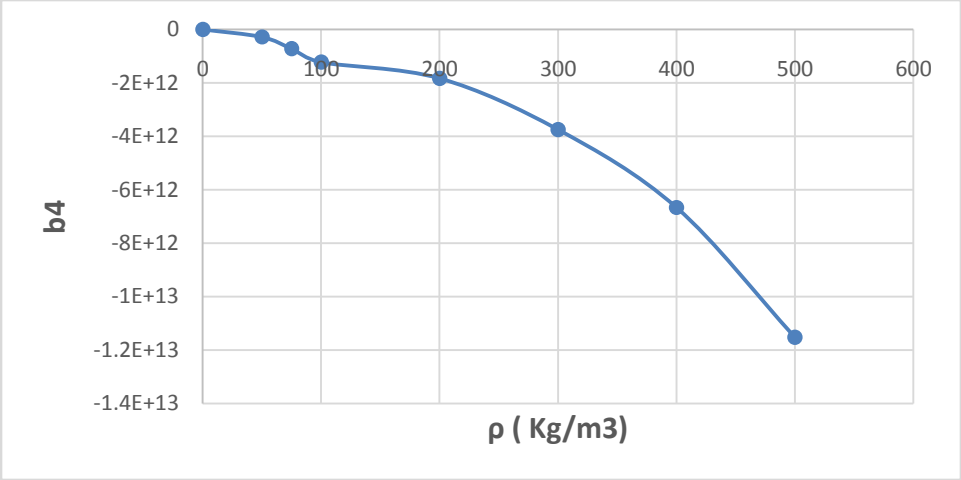


Figure (4.25): The relation between b4 and density for P vs1/T study of vapor phase (Gen. Data)

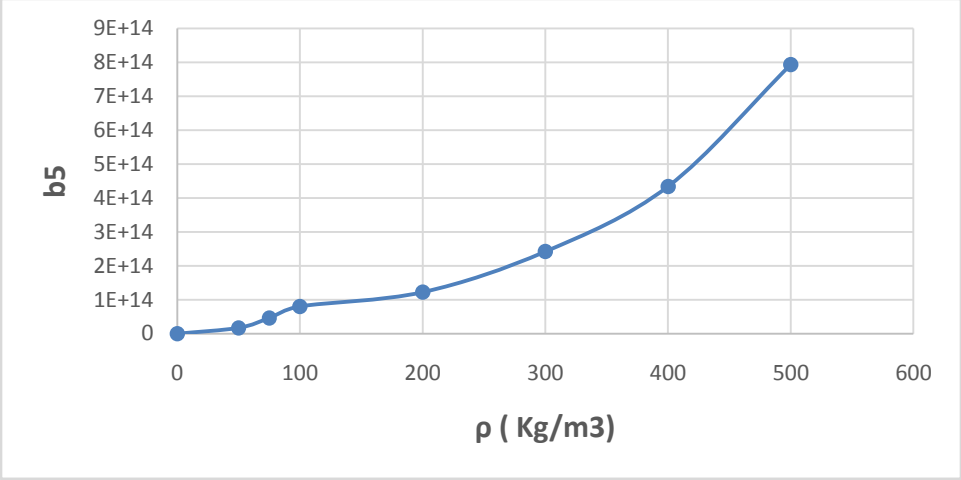


Figure (4.26): The relation between b5 and density for P,1/T of vapor phase (Gen. data)

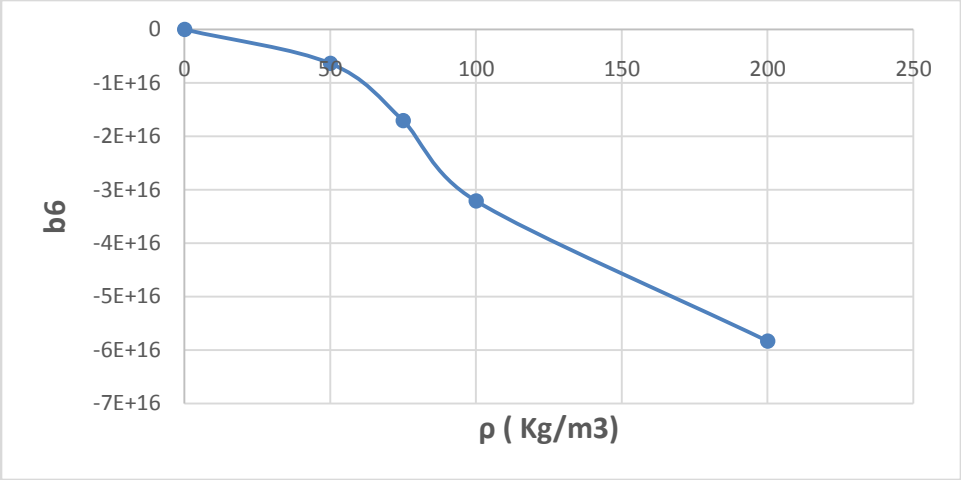


Figure (4.27): The relation between b6 and density for P,1/T of vapor phase (Gen. data)

Polymath was used then to get the second model. The seventh power equation had the following form:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 + c6\rho^6 + c7\rho^7 \quad \text{(4.15)}$$

By substituting equation (4.15) into equation (4.14), we get the following equation of state:

$$P = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5 + c16\rho^6 + c17\rho^7)\frac{1}{T} + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5 + c26\rho^6 + c27\rho^7)\frac{1}{T^2} + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5 + c36\rho^6\, c37\rho^7)\frac{1}{T^3} + (c41\rho + c42\rho^2 + c43\rho^3 + c44\rho^4 + c45\rho^5 + c46\rho^6 + c47\rho^7)\frac{1}{T^4} + (c51\rho + c52\rho^2 + c53\rho^3 + c54\rho^4 + c55\rho^5 + c56\rho^6 + c57\rho^7)\frac{1}{T^5} + (c61 + c62\rho^2 + c63\rho^3 + c64\rho^4)\frac{1}{T^6} \quad \text{(4.16)}$$

Polymath was used again to perform the global fit. Figures (4.27) and (4.28) show the residual and percentage error of the global fit respectively. And table (4.4) show the values obtained for the coefficients of model (4.16). We had 39 coefficients in the two variables model with 431 data points for temperature, pressure and density.

Table (4.4): Coefficients obtained of P vs 1/T study of vapor phase for the generated data

Variable	Initial guess	Value	95% confidence
a11	371.0513	381.2106	46.29265
a12	-1.521878	-1.926298	0.8831035
a13	0.0694059	0.072646	0.0043634
a14	-0.0006927	-0.0006919	1.84E-05
a15	3.44E-06	3.35E-06	6.88E-08
a16	-8.12E-09	-7.79E-09	1.76E-10
a17	7.18E-12	6.83E-12	1.82E-13
a21	-3.67E+05	-3.83E+05	6.79E+04
a22	1736.327	2403.302	1242.593
a23	-89.8418	-95.94139	4.647269
a24	0.8526929	0.8661192	0.0141111
a25	-0.0041366	-0.0040911	4.32E-05
a26	9.69E-06	9.45E-06	1.22E-07
a27	-8.52E-09	-8.22E-09	1.58E-10
a31	1.60E+08	1.70E+08	3.95E+07
a32	-7.37E+05	-1.16E+06	7.02E+05
a33	4.50E+04	4.91E+04	2164.316
a34	-393.5766	-406.9084	5.174755
a35	1.844891	1.853508	0.0163917
a36	-0.0042775	-0.0042325	4.33E-05
a37	3.73E-06	3.65E-06	7.06E-08
a41	-3.64E+10	-3.95E+10	1.14E+10
a42	1.30E+08	2.56E+08	2.00E+08
a43	-1.08E+07	-1.20E+07	6.97E+05
a44	8.19E+04	8.63E+04	1725.378
a45	-360.9889	-368.7153	5.120365
a46	0.8256107	0.8303924	0.0133051
a47	-0.0007122	-0.0007085	1.94E-05

Table (4.4): Continued.

Variable	Initial guess	Value	95% confidence
a51	4.23E+12	4.68E+12	1.63E+12
a52	-6.50E+09	-2.46E+10	2.89E+10
a53	1.23E+09	1.39E+09	1.41E+08
a54	-6.92E+06	-7.45E+06	3.75E+05
a55	2.61E+04	2.72E+04	783.6482
a56	-58.69645	-60.08491	2.133925
a57	0.0499022	0.0505309	0.0025231
a61	-1.99E+14	-2.24E+14	9.28E+13
a62	-3.17E+11	6.69E+11	1.71E+12
a63	-5.14E+10	-5.87E+10	1.15E+10
a64	1.06E+08	1.19E+08	3.07E+07

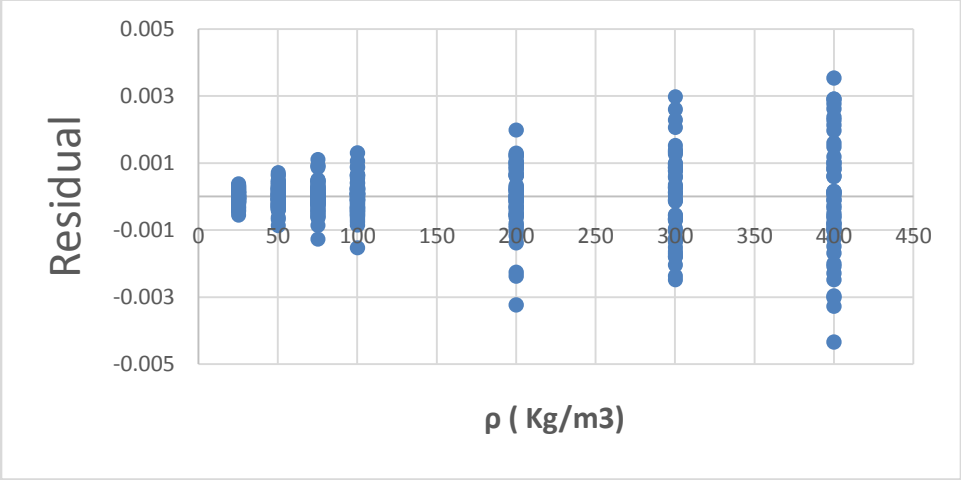


Figure (4.28): Global fit residual for P vs 1/T relation of vapor phase (Gen. Data)

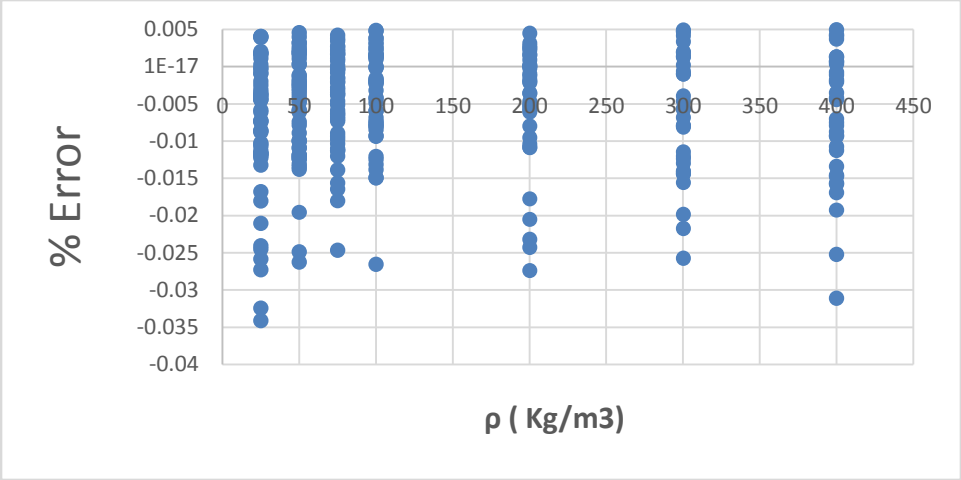


Figure (4.29): Global fit percentage error for P vs 1/T relation of vapor phase (Gen. Data)

According to figure (4.29), the percentage error obtained of this model was ± 0.04. However, the 95% confidence of the results has an error which doesn't exceed ± 0.01. That means this model obtains a deviation less than the random error imposed to the data. This model has less deviation than P Versus T model. That means P Versus 1/T study obtains less deviation than P Versus T study.

4.2.2 Liquid Phase Study

For the liquid part, I did the same procedure explained in the previous studies. The fifth power equation had the best fit to the data used. It had the following form:

$$P = b1T + b2T^2 + b3T^3 + b4T^4 + b5T^5 \quad \text{(4.17)}$$

Figures (4.30) to (4.34) show the relation between the coefficients and the density. It can be noted from the figures that four isochores were used in this study. The coefficients have four density data in addition to the origin point.

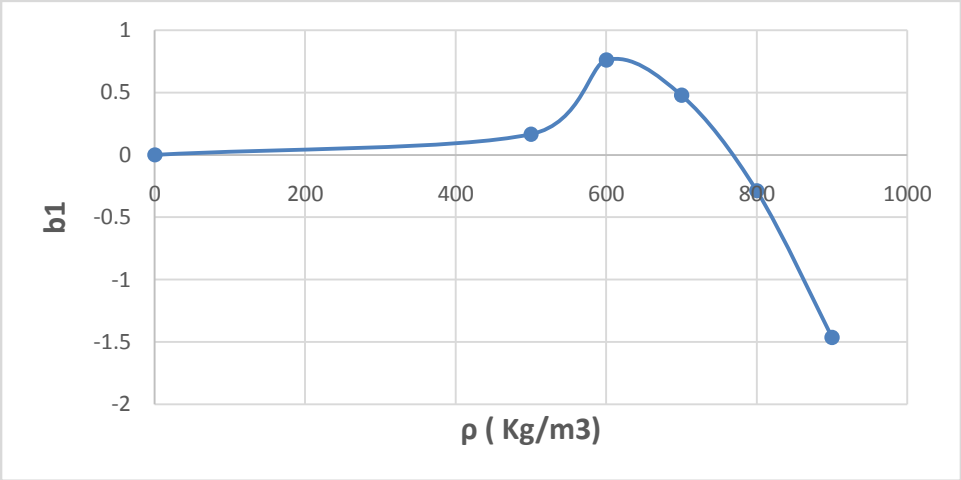


Figure (4.30): The relation between b1 and density for P vs T study of liquid phase (Gen. Data)

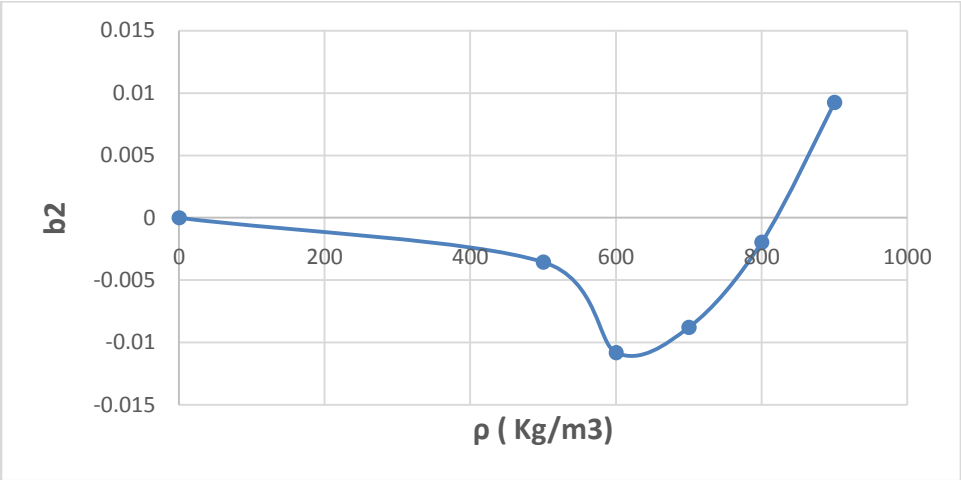


Figure (4.31): The relation between b2 and density for P vs T study of liquid phase (Gen. Data)

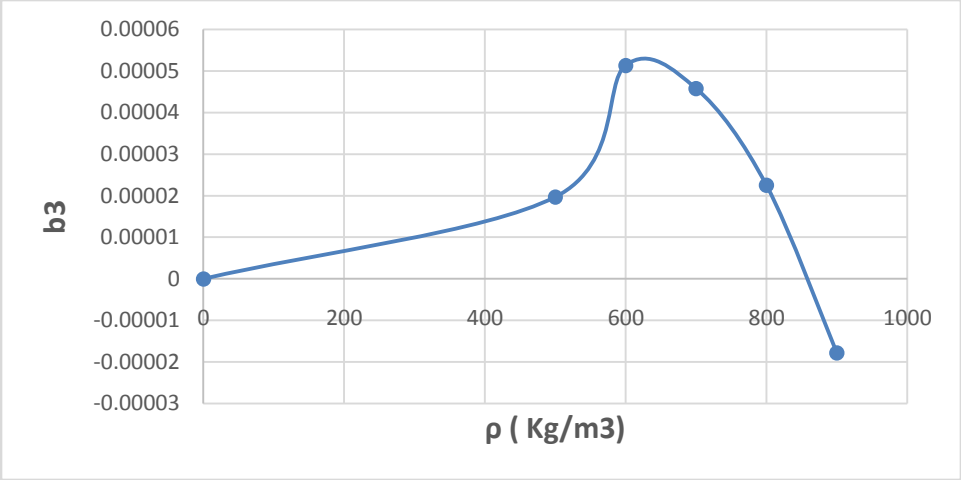


Figure (4.32): The relation between b3 and density for P vs T study of liquid phase (Gen. Data)

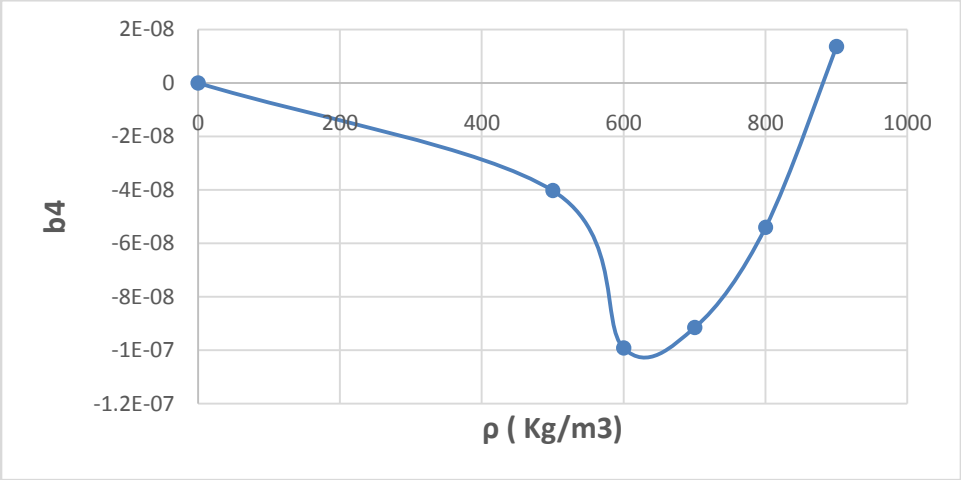


Figure (4.33): The relation between b4 and density for P vs T study of liquid phase (Gen. Data)

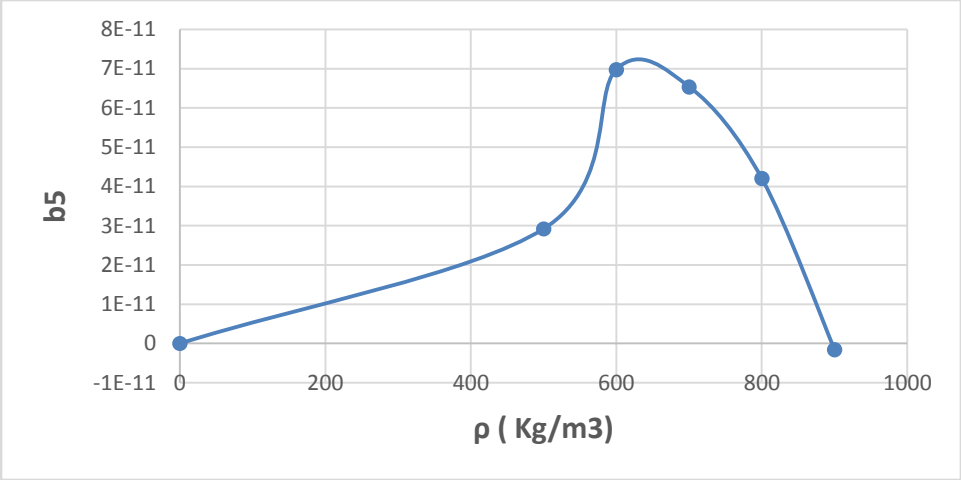


Figure (4.34): The relation between b5 and density for P vs T study of liquid phase (Gen. Data)

The dependence of the coefficients upon density came up with the following model, which had the best fit:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 \quad (4.18)$$

After substituting equation (7.18) into (4.17), we get the following equation of state:

$$P = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5)\,T + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5)T^2 + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5)T^3 + (c41\rho + c42\rho^2 + c43\rho^3 + c44\rho^4 + c45\rho^5)T^4 + (c51\rho + c52\rho^2 + c53\rho^3 + c54\rho^4 + c55\rho^5)T^5 \quad (4.19)$$

Polymath was used to perform the global fit. Figures (4.35) and (4.36) show the residual and percentage error of the global fit respectively. And table (4.5) show the values obtained for the coefficients of model (4.19). We had 25 coefficients in the two variables model with 260 data points for temperature, pressure and density.

Table (4.5): Coefficients obtained for P vs T study of liquid phase for the generated data

Variable	Initial guess	Value	95% confidence
a11	-0.1229391	-0.1227381	0.0081275
a12	0.000654	0.0006529	3.65E-05
a13	-1.27E-06	-1.27E-06	6.16E-08
a14	1.08E-09	1.08E-09	5.19E-11
a15	-3.48E-13	-3.47E-13	2.01E-14
a21	0.0013923	0.00139	7.60E-05
a22	-7.47E-06	-7.45E-06	3.06E-07
a23	1.46E-08	1.46E-08	4.46E-10
a24	-1.26E-11	-1.26E-11	4.00E-13
a25	4.08E-15	4.07E-15	1.96E-16
a31	-5.86E-06	-5.87E-06	2.75E-07
a32	3.16E-08	3.17E-08	1.00E-09
a33	-6.22E-11	-6.25E-11	1.37E-12
a34	5.40E-14	5.42E-14	1.66E-15
a35	-1.76E-17	-1.77E-17	9.27E-19
a41	1.10E-08	1.10E-08	4.95E-10
a42	-5.98E-11	-5.97E-11	1.96E-12
a43	1.19E-13	1.18E-13	3.69E-15
a44	-1.04E-16	-1.03E-16	4.61E-18
a45	3.40E-20	3.39E-20	2.27E-21
a51	-7.71E-12	-7.71E-12	3.86E-13
a52	4.21E-14	4.20E-14	1.85E-15
a53	-8.37E-17	-8.37E-17	4.10E-18
a54	7.35E-20	7.35E-20	4.73E-21
a55	-2.42E-23	-2.42E-23	2.08E-24

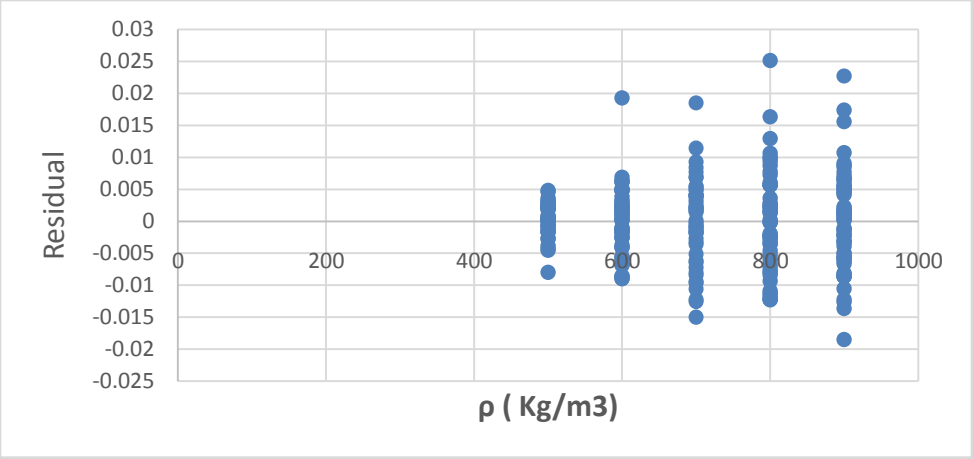


Figure (4.35): Global fit residual for P vs T study of liquid phase (Gen. Data)

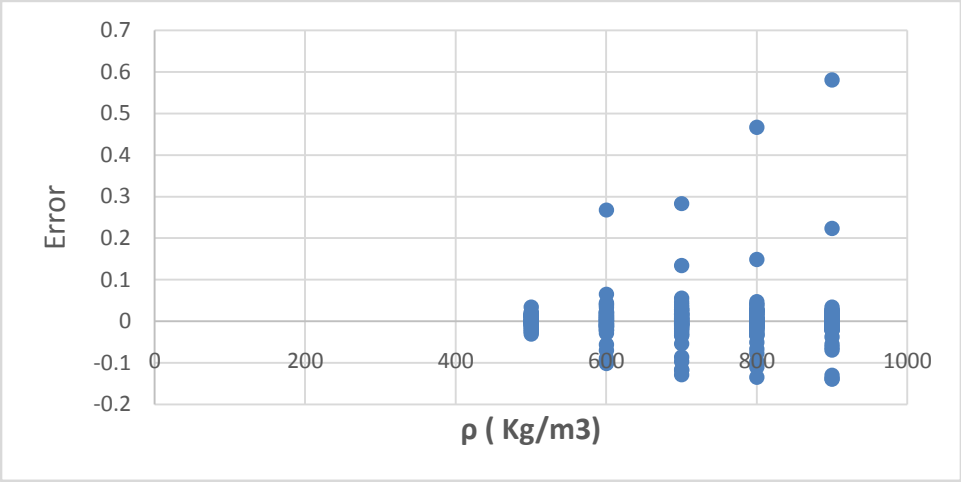


Figure (4.36): Global fit percentage error for P vs T study of liquid phase (Gen. Data)

According to figure (4.36), the percentage error obtained of this model was(-0.2 to 0.7) However, the 95% confidence of the results has an error which doesn't exceed ± 0.1. That means this model obtains a deviation within the random error imposed to the data. If we compare figure (4.36) to figure (4.21), we notice that the model covering the vapor phase of P versus T study had less deviation than the model covering liquid phase. That

is because these models are considered as a virial type equations of state, and it is more accurate in the vapor phase than in the liquid phase. In the liquid phase, the model is considered as a correlation only, but in the vapor phase the model has a physical meaning and considered as virial type equation of state.

4.2.3 Two Phases Study

After developing models to cover vapor and liquid phases separately, I was motivated to model an equation to cover the two phases. I studied the dependence of pressure upon temperature in liquid and vapor phases of carbon dioxide. Polymath 6.1 program was used to develop the most appropriate model to the data points I had in this study. I carried out the same procedure done before in the previous studies. The outcomes showed that, as the power of the model increases, we get better results. In other words, the error gets reduced as the model power increase. But, the weakness of this study occurs in having a systematic deviation in the residual, residual is the difference between the pressure inserted to the program and the pressure calculated from the model, plot. The good plots of residual as function of temperature should show random distribution instead of a trend. Thus, I had to study the dependence of (P-a0) upon temperature. Where a0 is the first coefficient of the model. But, in this study I had a problem of having (P – a0) data as negative values. And it is not possible to have negative values in the y-axes. So, this study was eliminated. In the third trial, I studied the dependence of (P-Psat) upon (1/T-1/Tsat). The deficiency of this study occurred in the insignificant coefficients. In the fourth and fifth power equations, I had some insignificant coefficients. Which means, the coefficients were outside the range of 2

sigma. The 95% confidence value was higher than the value of the coefficient. Thus this step was eliminated. In the fourth trial, I studied the dependence of (P-Psat) upon (1/T-Tsat). This study was eliminated as well because of the systematic deviation in the residual plot. In the fifth trial, I studied the dependence of (P-Psat) upon (T-Tsat). The residuals had random deviation, and all the coefficients were significant. Fourth power model had good results in this step. So, fourth power equation was used to describe the dependence of (P-Psat) upon (T-Tsat). The forth power model had the following form:

$$P = b1T + b2T^2 + b3T^3 + b4T^4 \quad (4.20)$$

The power of the fourth term was changed in order to have better representation of the residual plots. After many trails, the best power for the fourth term had to be 3.75. Thus, the model became as the following:

$$P = b1T + b2T^2 + b3T^3 + b4T^{3.75} \quad (4.21)$$

After that, I studied the dependence of the coefficients of model (4.21) upon density. Figures (4.37) to (4.40) show the relationship between the coefficients and density.

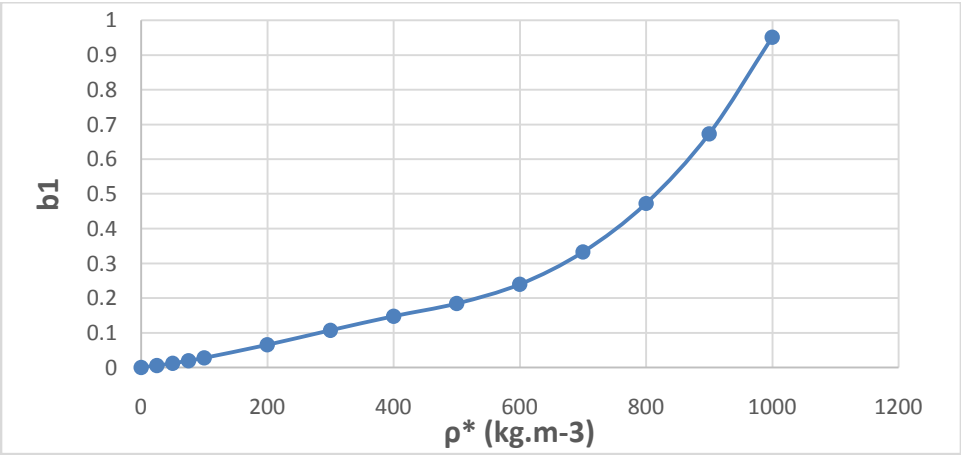


Figure (4.37): The relation between b1 and density for (P-Psa) vs (T-Tsat) study of two phases (Gen. Data)

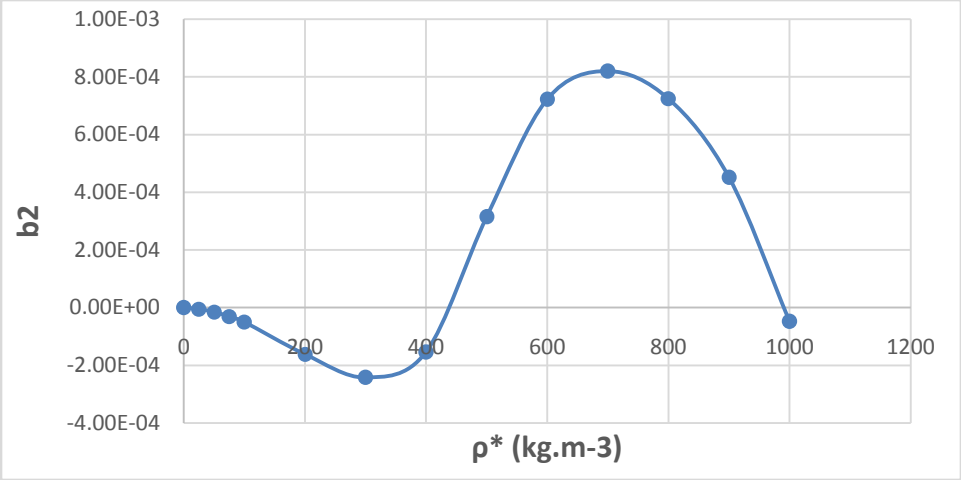


Figure (4.38): The relation between b2 and density for (P-Psa) vs (T-Tsat) study of two phases (Gen. Data)

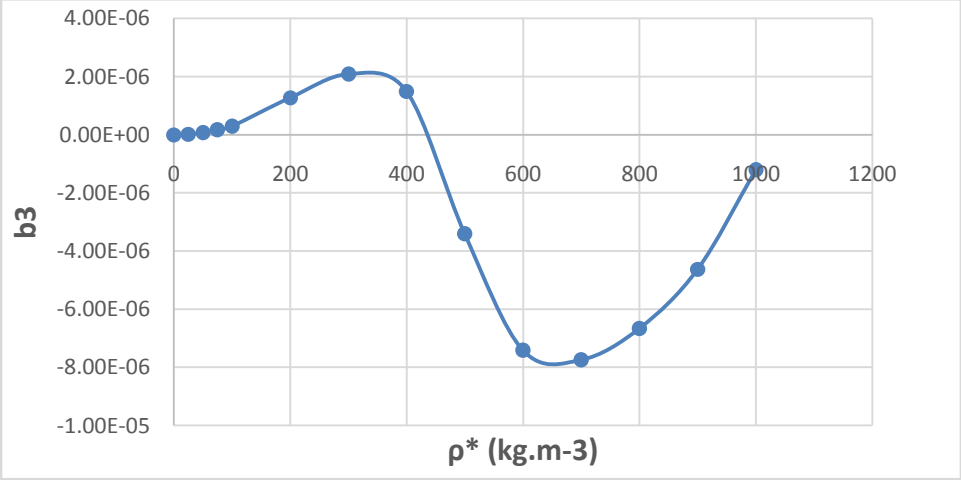


Figure (4.39): The relation between b3 and density for (P-Psa) vs (T-Tsat) study of two phases (Gen. Data)

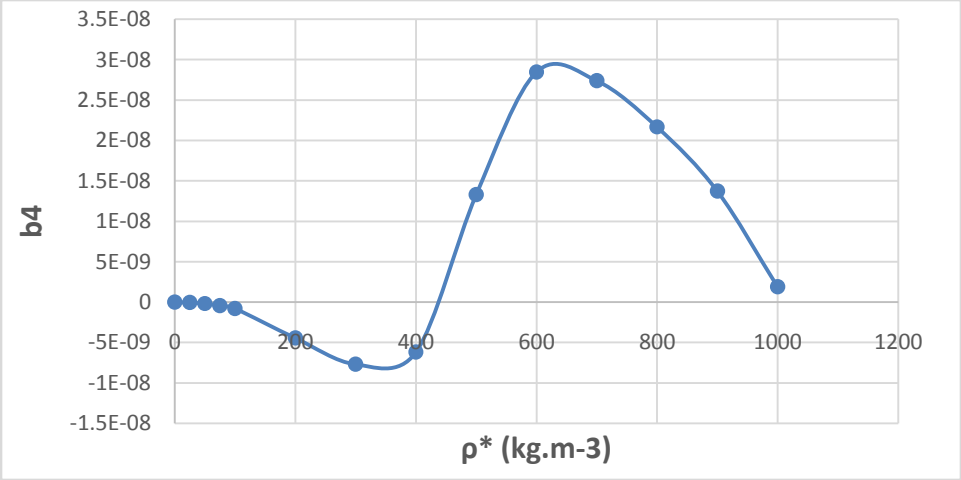


Figure (4.40): The relation between b4 and density for (P-Psa) vs (T-Tsat) study of two phases (Gen. Data)

After that, polymath program was used again to predict a model that has good fitting to the data points plotted above. The seventh power equation was chosen to describe the relation between the coefficients and density. The model predicted had the following form:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 + c6\rho^6 + c7\rho^7 \quad \text{(4.22)}$$

The first coefficient of b2, b3, and b4 were insignificant. So, I had to eliminate them before I perform the global fit to avoid any bad results. But, some other coefficients had to be eliminated in the second trial because they became insignificant. In this study, I had to eliminate the most insignificant coefficient and refit again until I get all the coefficients significant.

After substituting equation (4.22) into (4.2), we will get an equation of state expressed in pressure and function of temperature and density. The equation of state had the following form:

$$P - Psat = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5 + c16\rho^6 + c17\rho^7)\,(T - Tsat) + (c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5 + c26\rho^6 + c27\rho^7)(T - Tsat)^2 + (c32\rho^2 + c4\rho^4 + c35\rho^5 + c36\rho^6 + c37\rho^7)(T - Tsat)^3 + (c42\rho^2 + c43\rho^3 + c45\rho^5 + c46\rho^6)(T - Tsat)^{3.75} \quad (4.23)$$

In this global fit, I had 22 variables with 835 data points of (P-Psat), (T-Tsat) and density. Figures (4.41) and (4.42) show the residual and percentage error of the global fit respectively. Table (4.6) show the values obtained for the coefficients of model (4.13).

Table (4.6): Coefficients obtained of (P-Psat) vs. (T-Tsat) study of two phases for the generated data

Variable	Initial guess	Value	95% confidence
c11	0.0002035	0.000202783	1.02E-06
c12	5.74E-07	5.72606E-07	3.59E-08
c13	2.77E-09	2.76831E-09	3.22E-10
c14	-1.82E-11	-1.76094E-11	1.21E-12
c15	3.52E-14	3.37837E-14	2.14E-15
c16	-2.75E-17	-2.66096E-17	1.79E-18
c17	7.92E-21	7.84202E-21	5.67E-22
c22	-5.14E-09	-5.17041E-09	5.80E-10
c23	-3.11E-11	-3.15447E-11	4.68E-12
c24	2.47E-13	2.28029E-13	2.31E-14
c25	-4.77E-16	-4.33689E-16	4.60E-17
c26	3.71E-19	3.45502E-19	4.03E-20
c27	-1.04E-22	-1.03186E-22	1.31E-23
c32	7.99E-11	7.88998E-11	8.79E-12
c34	-1.11E-15	-1.13255E-15	1.25E-16

Table (4.6): Continued.

Variable	Initial guess	Value	95% confidence
c35	2.47E-18	2.34862E-18	2.94E-19
c36	-1.85E-21	-1.76249E-21	2.59E-22
c37	4.62E-25	4.66234E-25	8.31E-26
c42	-1.41E-12	-1.42016E-12	1.80E-13
c43	4.64E-15	4.59217E-15	4.84E-16
c45	-7.88E-21	-7.84502E-21	9.64E-22
c46	4.66E-24	4.68416E-24	6.51E-25

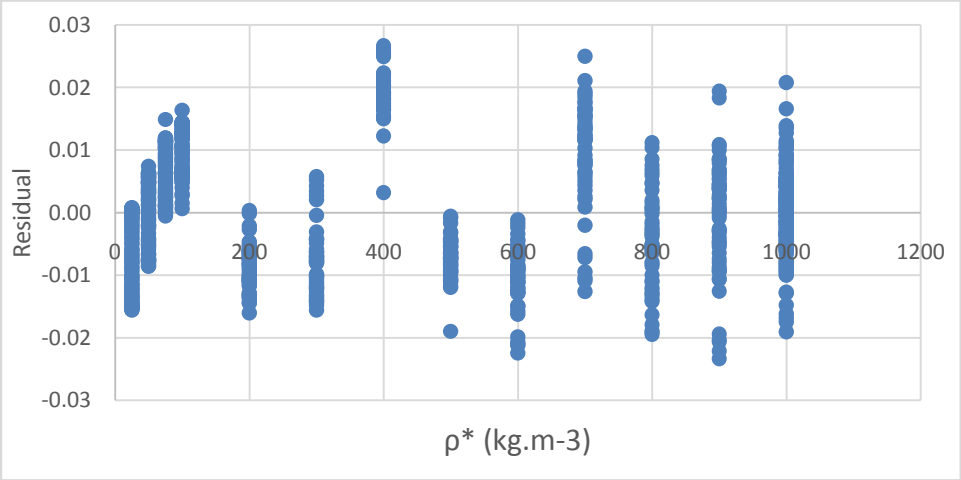


Figure (4.41): Global fit residual for (P-Psa) vs (T-Tsat) study of two phases (Gen. Data)

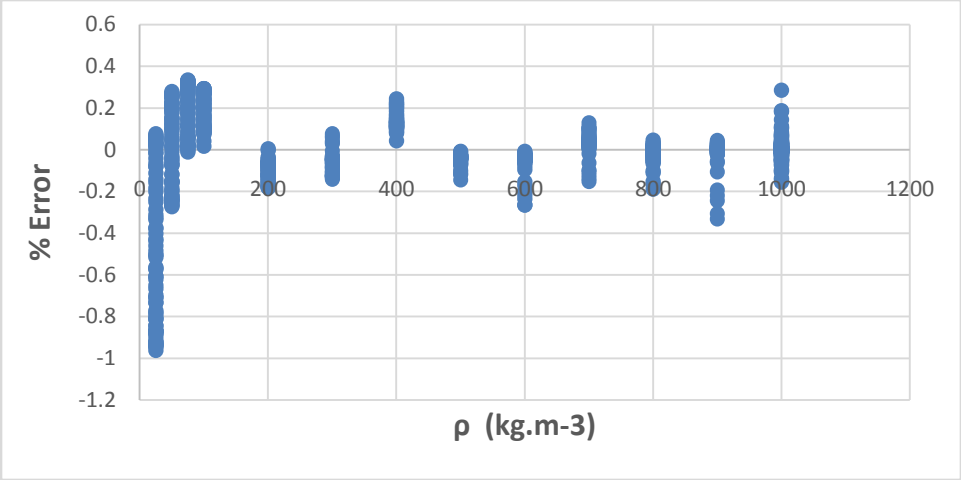


Figure (4.42): Global fit percentage error for (P-Psa) vs (T-Tsat) study of two phases (Gen. Data)

According to figure (4.42), the percentage error obtained of this model was(-1.0 to 0.4) However, weighted regression analysis can be used in this study to reduce the deviation significantly. By weighted regression analysis, we can increase the weightage of the first three isochores to reduce the error. This step would be done as a future work.

4.2.4 Liquid and Vapor Phases Separately

I developed two models for the vapor and liquid phases separately studying the dependence of (P-Psat) upon (T-Tsat). For the vapor phase study, the fifth power equation obtained the best fit having the following form:

$$P - Psat = b1(T - Tsat) + b2(T - Tsat)^2 + b3(T - Tsat)^3 + b4(T - Tsat)^4 + b5\,(T - Tsat)^5 \quad (4.24)$$

To get the second model, we have to plot the relation between the coefficients and the density. Figures (4.43) to (4.47) show the plots required to perform the second

regression analysis. It can be noted that each of the coefficients has seven data points of density in addition to the origin point.

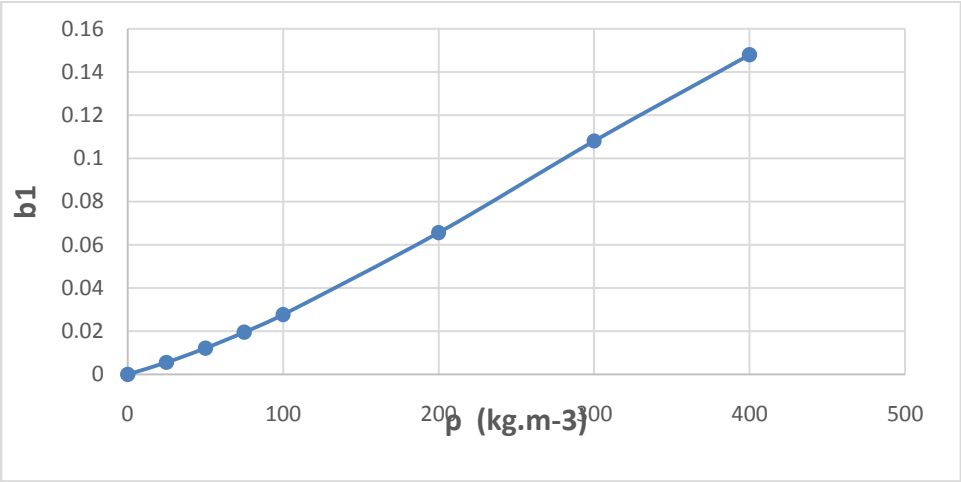


Figure (4.43): The relation between b1 and density for (P-Psat) vs (T-Tsat) study of vapor phase (Gen. Data)

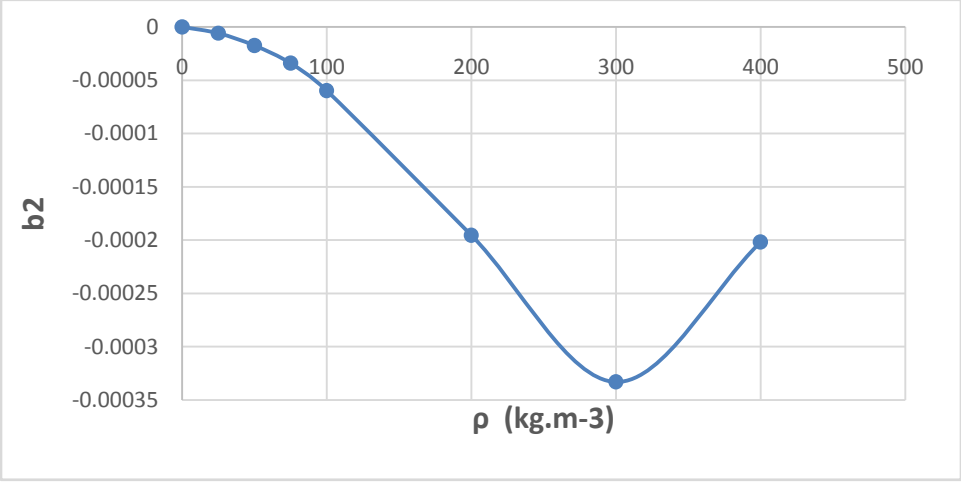


Figure (4.44): The relation between b2 and density for (P-Psat) vs (T-Tsat) relation of vapor phase (Gen. Data)

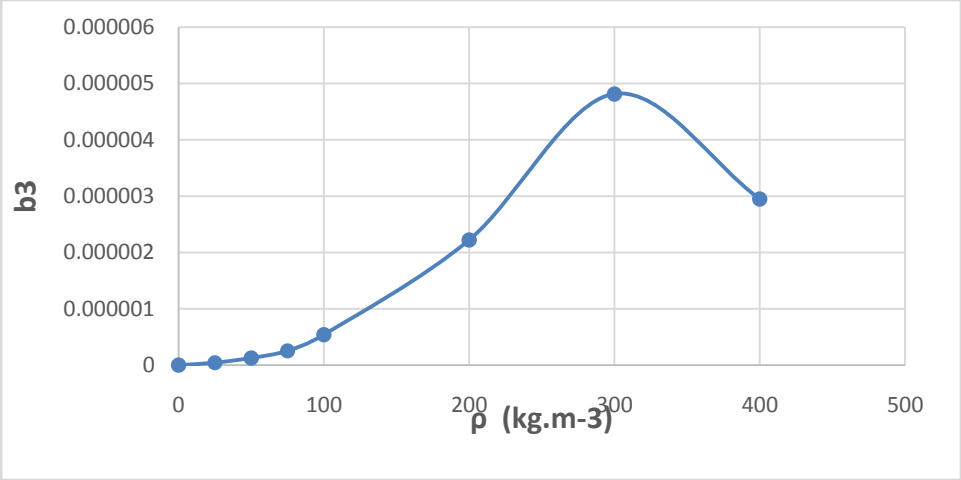


Figure (4.45): The relation between b3 and density for (P-Psat) vs (T-Tsat) study of vapor phase (Gen. Data)

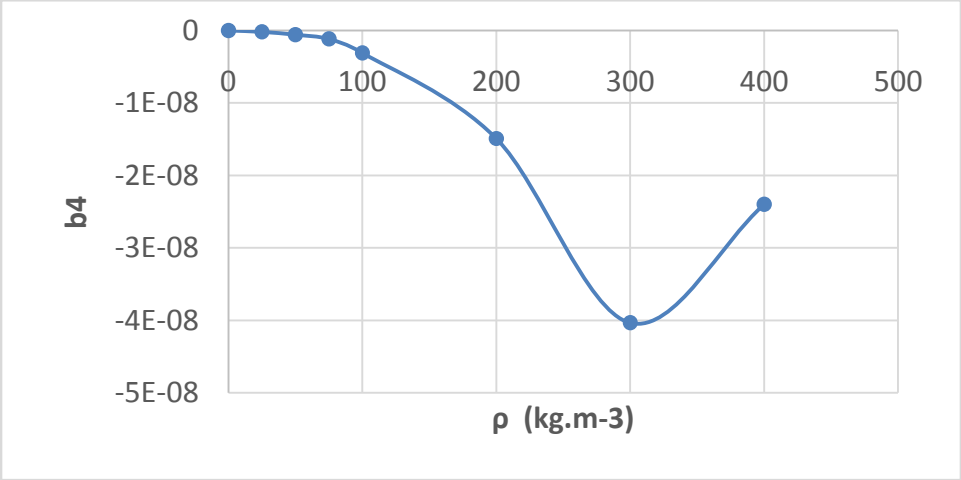


Figure (4.46): The relation between b4 and density for (P-Psat) vs (T-Tsat) study of vapor phase (Gen. Data)

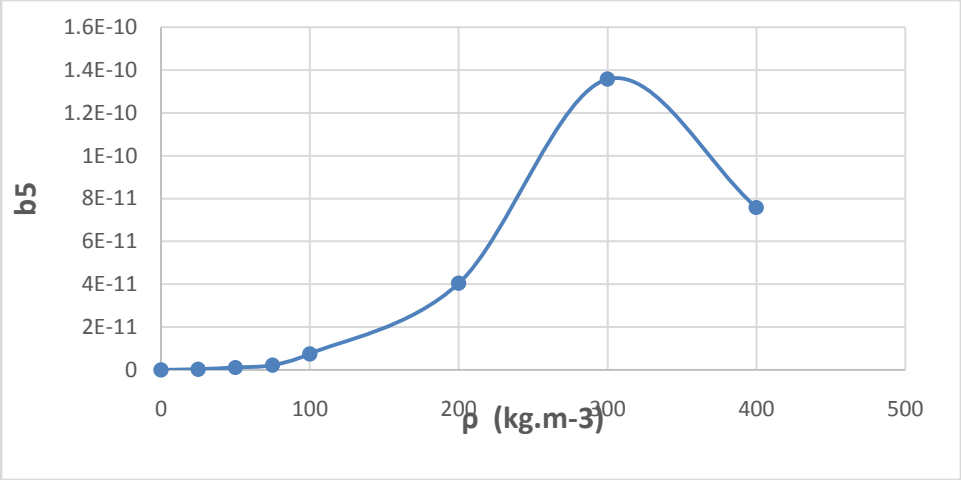


Figure (4.47): The relation between b5 and density for (P-Psat) vs (T-Tsat) study of vapor phase (Gen. Data)

The dependence of the coefficients upon density came up with the following equation:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 + c6\rho^6 + c7\rho^7 \quad \text{(4.25)}$$

After substituting equation (4.25) into equation (4.24), we get the following equation of state:

$$P - Psat = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5 + c16\rho^6 + c17\rho^7)\,(T - Tsat) + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5 + c26\rho^6 + c27\rho^7)(T - Tsat)^2 + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5 + c36\rho^6 + c37\rho^7)(T - Tsat)^3 + (c41\rho + c42\rho^2 + c43\rho^3 + c44\rho^4 + c45\rho^5 + c46\rho^6 + c47\rho^7)(T - Tsat)^4 + (c51\rho + c52\rho^2 + c53\rho^3 + c54\rho^3 + c55\rho^5 + c56\rho^6 + c57\rho^7)(T - Tsat)^5 \quad \text{(4.26)}$$

In this global fit, we had 35 coefficients and 424 data points of (P-Psat), (T-Tsat) and density. Figures (4.48) and (4.49) show the residual and percentage error of the global fit respectively. Table (4.7) show the values obtained for the coefficients of model (4.26).

Table (4.7): Coefficients obtained for (P-Psat) vs. (T-Tsat) study of vapor phase for the generated data

Variable	Initial guess	Value	95% confidence
a11	0.000195	0.000195	1.98E-05
a12	1.32E-06	1.32E-06	1.26E-06
a13	-1.11E-08	-1.11E-08	2.92E-08
a14	1.03E-10	1.03E-10	3.13E-10
a15	-5.33E-13	-5.32E-13	1.64E-12
a16	1.31E-15	1.31E-15	4.02E-15
a17	-1.20E-18	-1.20E-18	3.68E-18
a21	5.33E-08	5.24E-08	8.57E-07
a22	-1.92E-08	-1.92E-08	5.26E-08
a23	4.12E-10	4.13E-10	1.17E-09
a24	-5.06E-12	-5.07E-12	1.24E-11
a25	2.87E-14	2.88E-14	6.45E-14
a26	-7.36E-17	-7.41E-17	1.58E-16
a27	6.95E-20	6.99E-20	1.45E-19
a31	-3.26E-09	-3.28E-09	1.39E-08
a32	3.82E-10	3.83E-10	8.56E-10
a33	-1.00E-11	-1.01E-11	1.93E-11
a34	1.25E-13	1.26E-13	2.07E-13
a35	-7.12E-16	-7.13E-16	1.10E-15
a36	1.83E-18	1.84E-18	2.74E-18
a37	-1.74E-21	-1.74E-21	2.54E-21
a41	3.80E-11	3.86E-11	1.03E-10
a42	-3.65E-12	-3.69E-12	6.71E-12
a43	9.97E-14	1.01E-13	1.60E-13
a44	-1.24E-15	-1.25E-15	1.80E-15
a45	7.04E-18	7.11E-18	9.84E-18
a46	-1.82E-20	-1.83E-20	2.50E-20
a47	1.73E-23	1.74E-23	2.34E-23

Table (4.7): Continued

Variable	Initial guess	Value	95% confidence
a51	-1.40E-13	-1.40E-13	2.94E-13
a52	1.25E-14	1.25E-14	2.08E-14
a53	-3.47E-16	-3.47E-16	5.27E-16
a54	4.31E-18	4.30E-18	6.15E-18
a55	-2.45E-20	-2.45E-20	3.42E-20
a56	6.35E-23	6.34E-23	8.75E-23
a57	-6.05E-26	-6.04E-26	8.24E-26

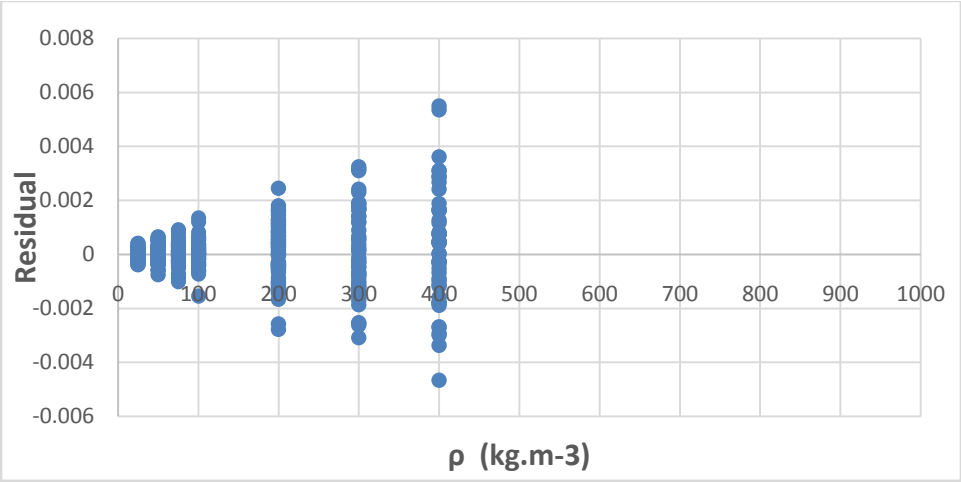


Figure (4.48): Global fit residual for (P-Psa) vs (T-Tsat) study of vapor phase (Gen. Data)

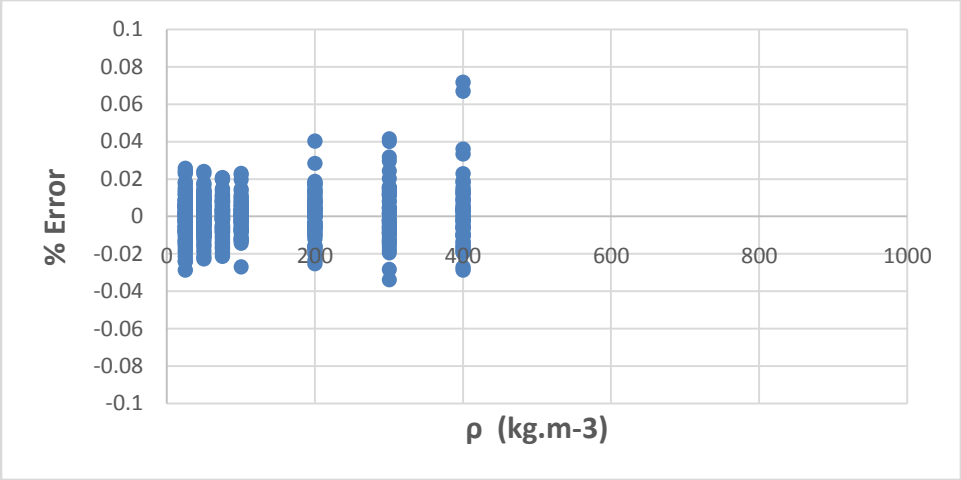


Figure (4.49): Global fit percentage error for (P-Psa) vs (T-Tsat) study of vapor phase (Gen. Data)

According to figure (4.49), the percentage error obtained of this model was(-0.04 to 0.08) However, the 95% confidence of the results has an error which doesn't exceed ± 0.04. That means this model obtains a deviation less than the random error imposed to the data.

For the liquid phase study, the fifth power equation obtained the best fit selected having the following form:

$$P - Psat = b1(T - Tsat) + b2(T - Tsat)^2 + b3(T - Tsat)^3 + b4(T - Tsat)^4 + b5\,(T - Tsat)^5 \quad (4.27)$$

To get the second model, we have to plot the relation between the coefficients and the density. Figures (4.50) to (4.54) show the plots. It can be noted from the figures that each coefficient has five data points for the density in addition to the origin point.

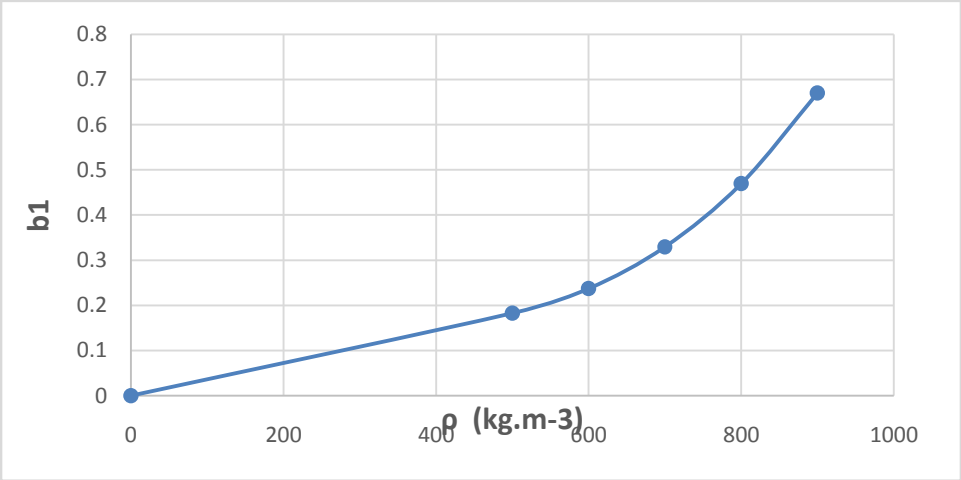


Figure (4.50): The relation between b1 and density for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

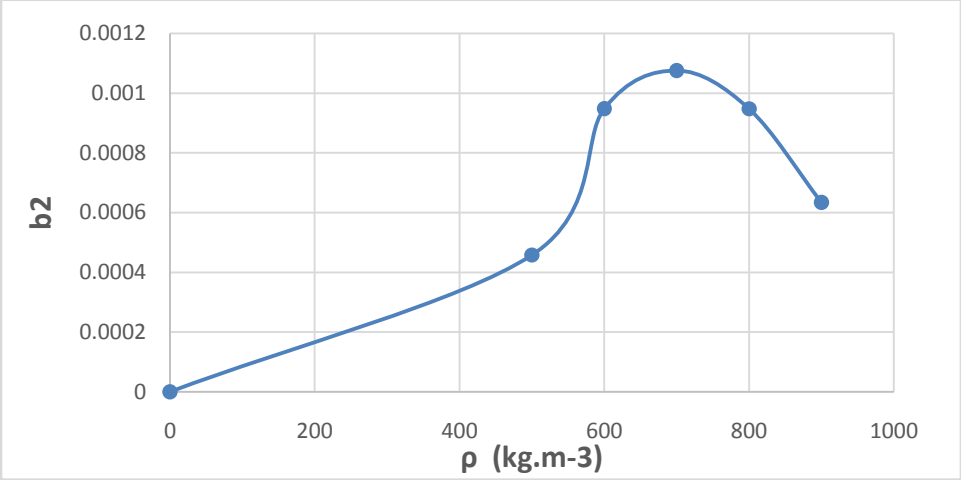


Figure (4.51): The relation between b2 and density for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

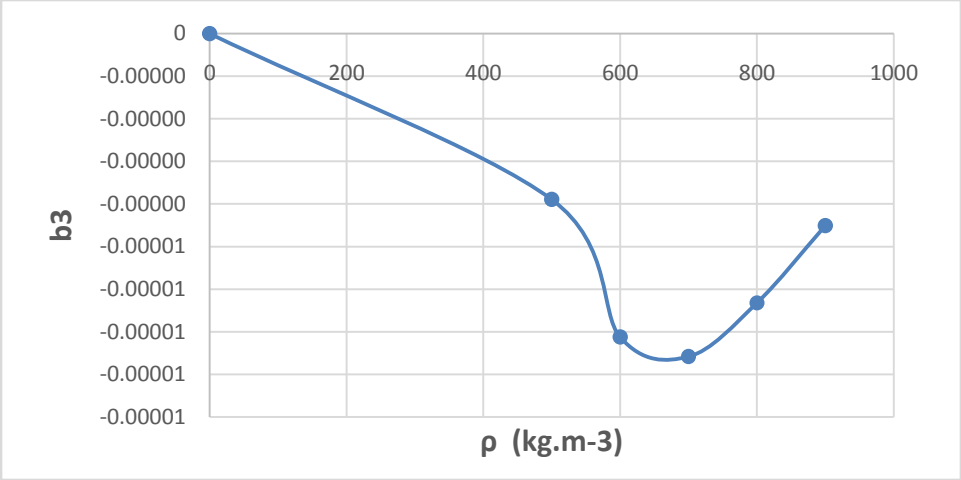


Figure (4.52): The relation between b3 and density for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

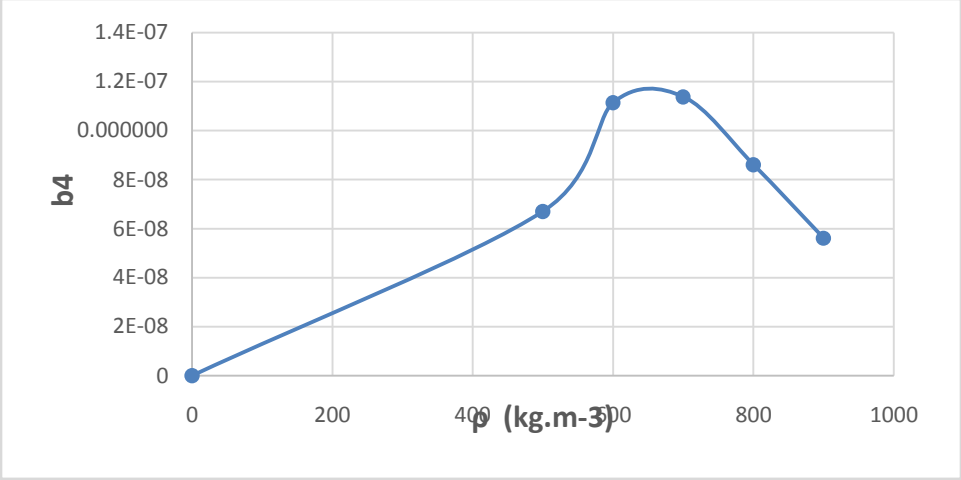


Figure (4.53): The relation between b4 and density for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

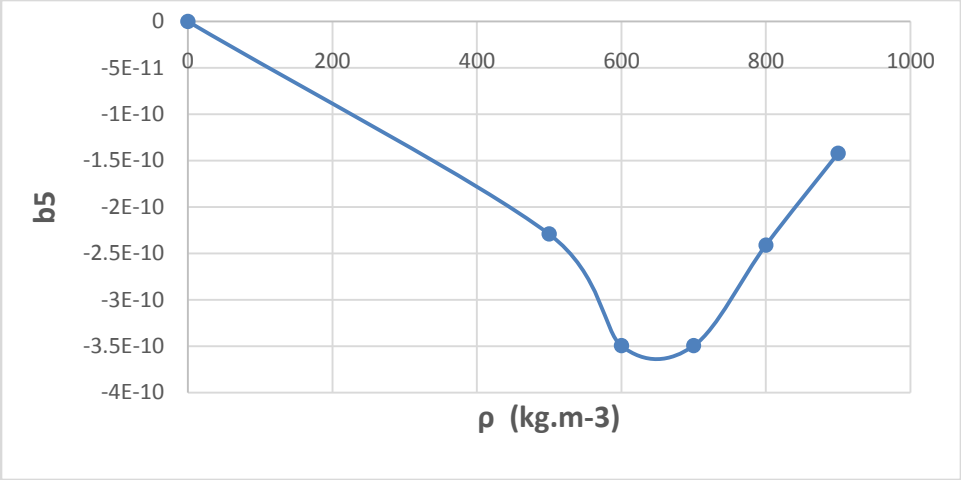


Figure (4.54): The relation between b5 and density for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

The dependence of the coefficients upon density came up with the following equation:

$$bi = c1\rho + c2\rho^2 + c3\rho^3 + c4\rho^4 + c5\rho^5 \quad (4.28)$$

After substituting equation (4.25) into equation (4.24), we get the following equation of state:

$$P - Psat = (c11\rho + c12\rho^2 + c13\rho^3 + c14\rho^4 + c15\rho^5)\,(T - Tsat) + (c21\rho + c22\rho^2 + c23\rho^3 + c24\rho^4 + c25\rho^5)(T - Tsat)^2 + (c31\rho + c32\rho^2 + c33\rho^3 + c34\rho^4 + c35\rho^5)(T - Tsat)^3 + (c41\rho + c42\rho^2 + c43\rho^3 + c44\rho^4 + c45\rho^5)(T - Tsat)^4 + (c51\rho + c52\rho^2 + c53\rho^3 + c54\rho^3 + c55\rho^5)(T - Tsat)^5 \quad (4.29)$$

In this global fit, we had 25 coefficients and 255 data points of (P-Psat), (T-Tsat) and density. Figures (4.55) and (4.56) show the residual and percentage error of the global fit respectively. Table (4.8) show the values obtained for the coefficients of model (4.29).

Table (4.8): Coefficients obtained of (P-Psat) vs. (T-Tsat) study of liquid phase for the generated data

Variable	Initial guess	Value	95% confidence
a11	0.0015039	0.0015038	4.47E-12
a12	-5.82E-06	-5.82E-06	5.60E-15
a13	1.02E-08	1.02E-08	6.73E-18
a14	-7.42E-12	-7.42E-12	7.90E-21
a15	2.53E-15	2.53E-15	9.12E-24
a21	-4.24E-05	-4.24E-05	5.06E-14
a22	2.14E-07	2.15E-07	6.18E-17
a23	-3.85E-10	-3.85E-10	7.31E-20
a24	3.04E-13	3.05E-13	8.47E-23
a25	-9.14E-17	-9.16E-17	9.71E-26
a31	5.11E-07	5.84E-07	5.16E-16
a32	-2.50E-09	-2.93E-09	6.18E-19
a33	4.17E-12	5.13E-12	7.20E-22
a34	-2.93E-15	-3.85E-15	8.28E-25
a35	7.41E-19	1.07E-18	9.42E-28
a41	-2.39E-09	-2.82E-09	4.98E-18
a42	1.02E-11	1.28E-11	5.86E-21
a43	-1.23E-14	-1.78E-14	6.76E-24
a44	3.20E-18	8.41E-18	7.71E-27
a45	1.32E-21	-4.92E-22	8.73E-30
a51	1.14E-12	1.19E-12	4.63E-20
a52	5.04E-15	4.62E-15	5.37E-23
a53	-4.26E-17	-4.15E-17	6.14E-26
a54	6.84E-20	6.71E-20	6.97E-29
a55	-3.23E-23	-3.18E-23	7.86E-32

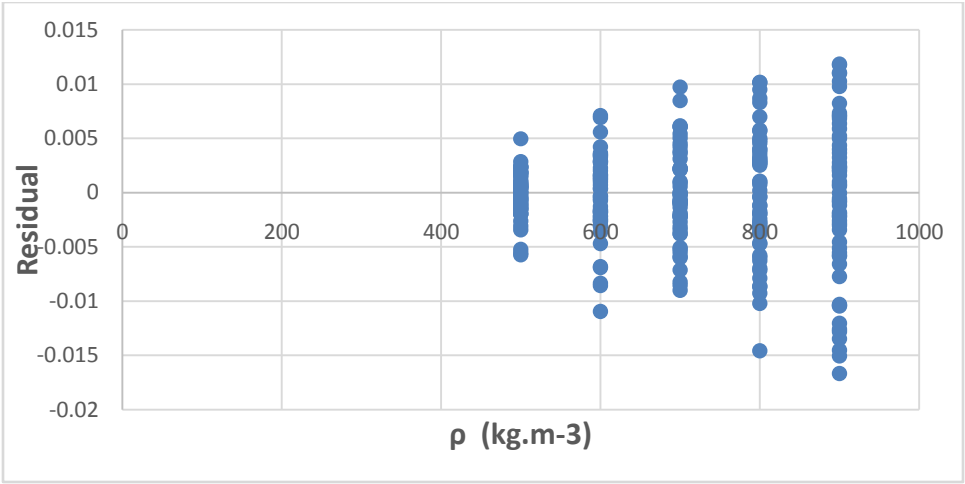


Figure (4.55): Global fit residual for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

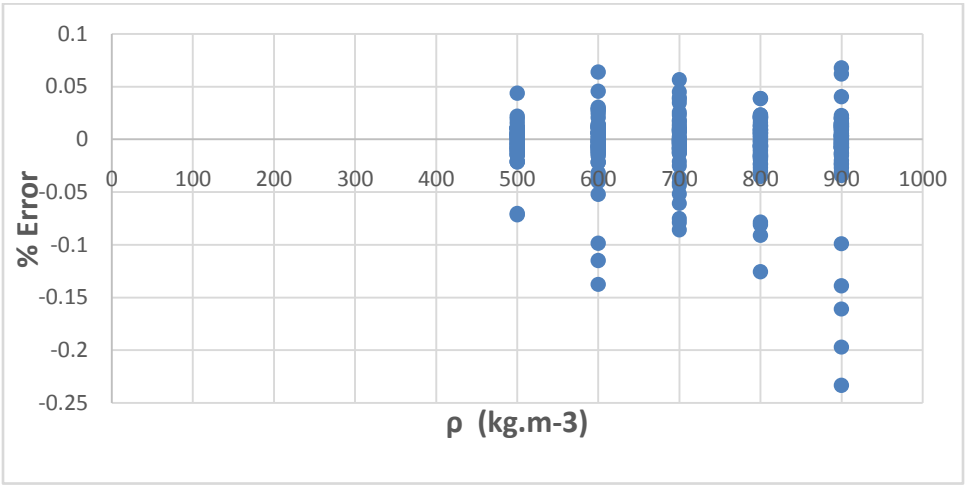


Figure (4.56): Global fit percentage error for (P-Psa) vs (T-Tsat) study of liquid phase (Gen. Data)

According to figure (4.56), the percentage error obtained of this model was (-0.25 to 0.1) However, the 95% confidence of the results has an error which doesn't exceed ± 0.1. That means this model obtains a deviation within the random error imposed to the data.

If we compare figure (4.56) to figure (4.49), we notice that the model covering the vapor phase of (P-Psat) versus (T-Tsat) study had less deviation than the model covering liquid phase. That is because these models are considered as a virial type equations of state, and it is more accurate in the vapor phase than in the liquid phase. In the liquid phase, the model is considered as a correlation only, but in the vapor phase the model has a physical meaning and considered as virial type equation of state.

5. DISCUSSION

For the experimental data global fit, I had two studies. The first global fit P (ρ, T) obtained quite good fit with residual ranging from (-0.02 to 0.02) and an error ranging from (-0.2to 0.2). The second global fit P (ρ, 1/T) obtained a residual ranging from (-0.008to 0.008) and an error ranging from (-0.1to 0.1). That means, having 1/T as independent variable obtains less error than having T for the experimental data.

For the generated data global fit, I had seven studies. The first two studies were only for the vapor phase studying the dependence of pressure upon T and 1/T. The dependence of P upon T obtained a residual ranging from (-0.008to 0.008) and an error ranging from (-0.04to 0.04). Whereas the dependence of P upon 1/T obtained a residual ranging from (-0.005to 0.005) and an error ranging from(-0.02to 0.005). That means, the dependence of pressure upon 1/temperature can obtain less error that the dependence of pressure upon temperature. For the liquid part, the dependence of pressure upon temperature study obtained a residual ranging from (-0.03to 0.03) and an error ranging from (-0.2to 0.2). The model covering the liquid region had more error than the model covering the vapor region. That was expected, because the virial type equation is better in predicting thermodynamic properties in the vapor region, and it's considered as physical model. But, in the liquid region the model developed was just a correlation.

For the two phase regions study, the global fit obtained a residual ranging from (-0.03to 0.03) and an error ranging from (-1.0to 0.4). This is quite large error compared to other studies. We notice that, in the first three isochores the error was larger than the rest. Because we don't have equal variance for all the isochores, as we should increase

the weightage of the more reliable observations. In the vapor phase, virial equation is more reliable than in the liquid phase. And small isochores data are more reliable than the large ones. The goal when using weighted least squares regression is to ensure that each data point has an appropriate level of influence on the final parameter estimates. Because of time constrain, this can be done as a future work. Since the goal of this project was not to develop an accurate model, rather to show a new technique in developing an equation of state. In the liquid part, the equation is just a correlation. It has a form of power series equation. But in the vapor part, the equation is physical and it is a viral type equation. I noticed that, the equation being predicted in the vapor phase can be used for any isochore in the vapor phase. But, for the liquid phase the equation predicted cannot be applied for the whole liquid region.

Finally, the last two studies were for liquid and vapor phases separately. I studied the dependence of (P-Psat) upon (T-Tsat) this time. For the vapor phase, the global fit obtained a residual ranging from (-0.006to 0.008) and an error ranging from (-0.05to 0.05). Whereas for the liquid phase, the global fit obtained a residual ranging from (-0.02to 0.015) and an error ranging from (-0.1to 0.1). The vapor phase study obtained less error than the liquid phase. That is the case always when we deal with a virial type equation. In summary, for both regions the error increased at the vicinity of the critical point no matter what kind of model we are dealing with.

6. CONCLUSION AND FUTURE WORK

In conclusion, it appears in this thesis that the percentage errors obtained for most of the studies were within the experimental and random error associated to the data. Thus, using isochoric data to model an equation of state is as adequate as using isothermal data. If we deal with the derivatives, isochoric slop is easier to fit than isothermal slop, and the isochors may be more useful, because the second derivative of the Helmholtz energy with respect to temperature gives the constant volume heat capacity. Experimentally, this property is measured using a calorimeter, which is relatively inaccurate. But, measuring Cv from the density is more accurate than the calorimeter measurements.

In this study, carbon dioxide data were used in the modeling, but this technique can extend to any component or mixture of components. This study shows that the proposed technique is good enough to include in equation of state development. It is possible to develop a simple equation of state using this technique, and nothing prevent its use to model more complex equations. The models proposed in this study resulted in virial type equations but, the technique can apply to other types of equations as well.

REFERENCES

(1) S. Ejaz, High Accuracy P, ρ, T Measurements of Pure Gas and Natural Gas Like Mixtures Using a Compact Magnetic Suspension Densimeter, PhD Dissertation, Texas A&M University, College Station, May 2007.

(2) Exxon Mobil, Summary Annual Report, 2012, www.exxonmobil.com/.../Files/news_pub_sar-2012.pdf

(3) Energy Information Administration, International Energy Outlook Report, 2011, http://www.eia.gov

(4) Energy Information Administration, Annual Energy Review, 2012, www.eia.org.

(5) P.V. Patil, Commissioning of a Magnetic Suspension Densitometer for High Accuracy Density Measurements of Natural Gas Mixtures, Ph.D. Dissertation, Texas A&M University, College Station, May 2005.

(6) Energy Information Administration, Annual Energy Outlook report with Projections to 2035, 2012, http://www.eia.gov

(7) Personal Communication to K.R. Hall, Texas A&M University at Qatar, 2012-2013.

(8) Exxon Mobil, The Outlook for Energy: A View to 2040, 2012. www.exxonmobil.com/Corporate/files/news_pub_eo.pdf

(9) International Energy Agency, Key World Energy Statistics ,2012, www.iea.org

(10) J. Zhou, Automatic Isochoric Apparatus for PVT Phase Equilibrium Studies of Natural Gas Mixtures, Ph.D. Dissertation, Texas A&M University, College Station, May 2005.

(11) M. Atilhan, M. High-Accuracy P-ρ-T Measurements up to 200 MPa Between 200 K to 500 K Using a Single Sinker Magnetic Suspension Densitometer for Pure and Natural Gas Like Mixtures. PhD. Dissertation, Texas A&M University, College Station, August 2007.

(12) Widia, Variation of Density with Composition for Natural Gas Mixtures in the Supercritical Region, MS Thesis, Texas A&M University, College Station, August 2003.

(13) BP Statistical Review of World Energy ,2013, www.bp.com/statistical review

(14) D. Rachovich, World's Top 15 Natural Gas Proven Reserve Holders, Estimated Proved Reserves of Natural Gas ,2012, http://petroleuminsights.blogspot.com/2012/01/worlds-top-15-natural-gas-proven.html#.UfT-AV_fpMs

(15) Energy Information Administration, Overview Data for Qatar, 2013, http://www.eia.gov/countries/cab.cfm?fips=QA,

(16) M. Economides, D. Wood, The State of Natural Gas, Journal of Natural Gas Science and Engineering. 1, 1-13, May 2009.

(17) General Secretarial for Development Planning, Qatar Economic Outlook 2011-2012, Oct 2011, www.gsdp.gov.qa

(18) General Secretarial for Development Planning, Qatar National Development Strategy 2011-2016, March 2011, www.gsdp.gov.qa

(19) Ministry of Business and Trade Investment Promotion Department, Rise with Qatar, 2011, www.mbt.gov.qa

(20) I. Ibrahim, F. Harrigan, Qatar's Economy: Past, Present and Future, Review article, September 2012.

(21) Global LNG Capacities Rising to Meet Increasing Demand, March 2011, http://www.ogj.com/articles/print/volume-109/issue10/transportation/special-report-global-lng-capacities-rising-to-meet.html

(22) Liquefied Natural Gas (LNG), QP Operations, 2013, http://www.qp.com.qa/en/Homepage/QPActivities/QPOperations.aspx

(23) O. Kunz, R. Klimeck, W. Wagner, M. Jaeschke, The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures, 2007.

(24) Personal Communication to Mert Atilhan, University of Qatar, 2012-2013.

(25) C. Linde, Natural Gas Processing Plants Linde Group, Engineering Division, Germany, 2013, www.linde.com

(26) A. Younger, Natural Gas Processing Principles and Technology – Part 1, University of Calgary, April 2004.

(27) D. Winterbone, Advanced Thermodynamics for Engineers, Thermodynamics and Fluid Mechanics Division, UMIST, Published by Arnold and Wiley, Chapter 8.

(28) M. Stewart and K. Arnold, Gas Sweetening and Processing Field Manual, Third Edition, Elsevier, 2011.

(29) J. Gallagher, Natural Gas Measurement Handbook, Published by Gulf Publishing Company Houston, Texas, 2006.

(30) C. Kimberly and T. John, Selection of Hydrate Suppression Methods for Gas Streams, Bryan Research and Engineering, Technical Papers, Bryan Research & Engineering, Bryan, Texas, 1997.

(31) B. Tohidi, Gas Hydrate Challenges in Oil and Gas Industry, Center of Gas Hydrate Research Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, UK.

(32) S. Ejaz, High Accuracy P-ρ-T Measurements of Pure Gas and Natural Gas like Mixtures Using a Compact Magnetic Suspension Densimeter, Ph.D. Dissertation, Texas A&M University, College Station, May 2007.

(33) D. E. C. Blanco, Experimental Characterization and Molecular Study of Natural Gas Mixtures, Ph.D. Dissertation, Texas A&M University, College Station, May 2010.

(34) M. Assel, N. Castro, C.A. and W. Wakeham, The Estimation of Physical Properties of Fluids, Part II, the Economic Advantage of Accurate Transport Property Data 1978.

(35) Mert Atilhan, A New Cubic Equation of State, A Master Thesis, Texas A&M University, College Station, May 2004.

(36) J. Valderrama, The State of the Cubic Equations of State, Industrial & Engineering Chemistry Research.42, 1603-1618, 2003.

(37) Van der Waals, On the Continuity of the Gaseous and Liquid States. Ph.D. Dissertation, University of Leiden, The Netherlands, 1873.

(38) T. Hill, An Introduction to Statistical Thermodynamics, Addison Wesley, Reading, Mass, 1960, retrieved by http://www.worldcat.org/title/introduction-to-statistical thermodynamics/oclc/248209.

(39) O. Redlich and J. N. S. Kwong, An Equation of State. Fugacities of Gaseous Solutions, 44, 233-244, 1949, http://pubs.acs.org/doi/abs/10.1021/cr60137a700

(40) G. Soave, Equilibrium constants from a modified RK equation of state Chemical Engineering Science. 27, 1197-1203, 1972. http://www.sciencedirect.com/science/article/pii/0009250972800964

(41) D. Peng and D. B. Robinson, A New Two Constant Equation of State, Industrial and Engineering Chemistry, Industrial and Engineering Chemistry Fundamentals, 15, 59–64 1976, http://pubs.acs.org/doi/abs/10.1021/i160057a011

(42) A. Goodwin, J. Sengers, and C. Peters, Applied Thermodynamics of Fluids, Published by The Royal Society of Chemistry, 2010.

(43) N. C. Patel and A. S. Teja, A New Cubic Equation of State for Fluids and Fluid Mixtures, Chemical Engineering Science. 37, 463–473, 1982. http://www.sciencedirect.com/science/article/pii/0009250982800997

(44) Xu, D.; Danesh, A.; Todd, A. C.; Stewart, G. Comparative Study of Cubic Equations of State for Predicting Phase Behavior and Volumetric Properties of North Sea Reservoir Oils. Presented at the International Conference on PVT Properties of Hydrocarbon System, Cranfield, U.K., 1989.

(45) A. Danesh, D. Xu, A. Todd, Comparative Study of Cubic Equations of State for Predicting Phase Behavior and Volumetric Properties of Injection Gas-Reservoir Oil Systems. Fluid Phase Equilibia. 63, 259, 1991.

(46) A. Danesh, D. Xu, A. Todd, Improving Predictions of EOS by Modifying Its Parameters for Supercritical Components of Hydrocarbons Reservoir Fluids. Fluid Phase Equilibria. 112, 45, 1994.

(47) J. Valderrama, P. Arce, A. Ibrahim, Vapor-Liquid Equilibrium in Hydrogen Sulfide-Hydrocarbon Mixtures. The Canadian Journal of Chemical Engineering**.** 77, 1239, 1999.

(48) R. Klimeck, R. Span, R. Kleinrahm, W. Wagner, Fundamental Equation for Calorific Properties. Ruhr-University Bochum, Germany, 1996.

(49) Equations of State and PVT Analysis, Applications for Improved Reservoir Modeling by Gulf Publishing Company, Houston, Texas, 2007.

(50) S. Huang, M. Radosz, Equation of State for Small, Large, Poly-disperse, and Associating Molecules: Extension to Mixtures, Industrial and Engineering Chemistry Research, 30, 1994-2005, 1991.

(51) J, Gross, G. Sadowski, Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules, Industrial and Engineering Chemistry Research, 40, 1244-1260, 2001

(52) K. Onnes, On the Lowest Temperature Yet Obtained, , Comm. Phys. Lab. Univ. Leiden, The Netherlands, 1922.

(53) J. Van Laar, About Vapor Tensions of Binary Mixtures. Journal of Physical Chemistry, 72, 723–751, 1910.

(54) J. Gmehling, K. Fischer, J. Li, And M. Schiller, Status and Results of Group Contribution Methods, Pure and Applied Chemistry, 65, 919–926, 1993. http://www.iupac.org/publications/pac/65/5/

(55) M. Huron, J. Vidal, New Mixing Rules in Simple Equations of State for Representing Vapour Liquid Equilibria of Strongly Non-Ideal Mixtures. Fluid Phase Equilibria, 3, 255–271, 1979. http://www.sciencedirect.com/science/article/pii/0378381279800011

(56) R. Heidemann, Excess Free Energy Mixing Rules for Cubic Equations of State. Fluid Phase Equilibria, 116, 454–464, 1996. http://www.sciencedirect.com/science/article/pii/0378381295029184

(57) H. Orbey, S. Sandler, On the Combination of Equation of State and Excess Free Energy Models, Fluid Phase Equilibria, 111, 53–70, 1995.

(58) M. Jaeschke, A. Humphreys, Standard GERG Virial Equation for Field Use, VDI-Verlag GmbH, 6, 1992.

(59) G. Silva, A New Equation of State: Theory and Experiment, Ph.D. Dissertation, Texas A&M University, Collage Station, 1987.

(60) O. Kunzand W. Wagner, The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004, Journal of chemical engineering data 2012.

(61) M. Jaeschke, P. Schley, Calculation of the Compressibility Factor of Natural Gases with the AGA8-DC92 Equation of State II Compared With Measured Values, 137, 20-425, 1996.

(62) Natural gas Calculation of Compression Factor Part 2, Calculation Using Molar-Composition Analysis; ISO Copyright Office: Geneva, 2005.

(63) E. Lemmon, D. Ortiz-Vega, K. Starling, K. Hall, W. Wagner, Deviations Between the AGA- 8 and GERG-2008 Equations of State for Natural Gases, Natural Gas Sampling Technology Conference (NGSTech), New Orleans, LA, January 2011.

(64) O. Kunz, R. Klimeck, W. Wagner, M. Jaeschke, The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures, 2007.

(65) J. Holste, K. Hall, P. Eubank, G. Esper, M. Watson, W. Warowny, D. Bailey, J. Young, and M. Bellomy, Experimental (p, V_m, T) for Pure CO_2 Between 220 and 450 K, Journal of Chemical Thermodynamics, 19, 1233 – 1250, 1987.

(66) E. Lemmon, M. Huber, M. McLinden, Reference Fluid Thermodynamic and Transport Properties-REFPROP,Version 9.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2010.

(67) S. Chatterjee and A. Hadi, Regression Analysis by Example, Fourth Edition. Copyright John Wiley & Sons, Inc, 2006.

(68) R. Mason, R. Gunst, and J. Hess, Statistical Design and Analysis of Experiments, second edition, Copyright John Wiley & Sons, Chapter 14, Linear Regression with One Predictor Variable, 2003.

APPENDIX A: EXPERIMENTAL DATA TABLES

Excel program fitting- 1st Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I1	4.482E+02		9.203E+00	-3.573E-02	1.277E-03	5.246E-03	2.752E-05	-3.842E-03	1.476E-05	1.514E+00	2.292E+00
	4.232E+02		8.495E+00	-4.893E-03	2.395E-05	-4.890E-03	2.392E-05	-2.397E-03	5.745E-06	1.203E+00	1.447E+00
	3.982E+02		7.779E+00	1.878E-02	3.528E-04	-5.801E-03	3.365E-05	-2.803E-03	7.859E-06	9.428E-01	8.889E-01
	3.732E+02		7.054E+00	3.312E-02	1.097E-03	3.345E-04	1.119E-07	-1.733E-03	3.005E-06	7.284E-01	5.305E-01
	3.482E+02		6.310E+00	2.870E-02	8.234E-04	4.111E-03	1.690E-05	-3.076E-03	9.465E-06	5.498E-01	3.023E-01
	3.232E+02		5.549E+00	6.999E-03	4.899E-05	7.006E-03	4.909E-05	1.570E-04	2.464E-08	4.097E-01	1.679E-01
	2.982E+02		4.756E+00	-4.697E-02	2.206E-03	-5.993E-03	3.592E-05	-1.540E-03	2.371E-06	2.962E-01	8.773E-02
					1.166E-03		4.678E-05		1.441E-05		2.858E+00
				S Deviation	3.414E-02		6.839E-03		3.796E-03		1.691E+00

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I1	4.482E+02	2.231E-03	9.203E+00	2.184E-01	4.770E-02	2.213E-02	4.899E-04	1.678E-03	2.815E-06	2.228E-04	4.965E-08	-8.664E-05	7.506E-09
	4.232E+02	2.363E-03	8.495E+00	2.965E-02	8.791E-04	-1.384E-02	1.916E-04	-2.780E-03	7.730E-06	-5.006E-04	2.506E-07	3.901E-04	1.522E-07
	3.982E+02	2.512E-03	7.779E+00	-1.010E-01	1.021E-02	-2.178E-02	4.743E-04	-1.020E-03	1.041E-06	-1.200E-04	1.441E-08	-7.190E-04	5.170E-07
	3.732E+02	2.680E-03	7.054E+00	-1.627E-01	2.648E-02	-7.322E-03	5.362E-05	3.057E-03	9.345E-06	1.256E-03	1.578E-06	6.932E-04	4.805E-07
	3.482E+02	2.872E-03	6.310E+00	-1.479E-01	2.187E-02	1.239E-02	1.534E-04	3.313E-04	1.098E-07	-1.358E-03	1.843E-06	-3.676E-04	1.351E-07
	3.232E+02	3.095E-03	5.549E+00	-3.294E-02	1.085E-03	2.384E-02	5.685E-04	-1.887E-03	3.561E-06	5.943E-04	3.532E-07	1.013E-04	1.027E-08
	2.982E+02	3.354E-03	4.756E+00	1.965E-01	3.861E-02	-1.542E-02	2.377E-04	6.216E-04	3.864E-07	-9.491E-05	9.007E-09	-1.130E-05	1.276E-10
					2.937E-02		5.423E-04		8.329E-06		2.049E-06		1.276E-10
				S Deviation	1.714E-01		2.329E-02		2.886E-03		1.431E-03		1.130E-05

Excel program fitting- 2nd Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 2	4.482E+02		6.411E+00	-1.687E-02	2.845E-04	2.480E-03	6.151E-06	-4.190E-03	1.755E-05	-1.221E+00	1.492E+00
	4.232E+02		5.962E+00	-2.117E-03	4.480E-06	-2.121E-03	4.501E-06	-2.512E-03	6.308E-06	-9.713E-01	9.434E-01
	3.982E+02		5.510E+00	8.741E-03	7.640E-05	-2.875E-03	8.268E-06	-2.727E-03	7.434E-06	-7.609E-01	5.789E-01
	3.732E+02		5.053E+00	1.544E-02	2.383E-04	-4.836E-05	2.338E-09	-2.260E-03	5.107E-06	-5.863E-01	3.437E-01
	3.482E+02		4.587E+00	1.285E-02	1.652E-04	1.238E-03	1.534E-06	-3.394E-03	1.152E-05	-4.463E-01	1.992E-01
	3.232E+02		4.115E+00	4.804E-03	2.308E-05	4.801E-03	2.305E-05	5.291E-04	2.799E-07	-3.293E-01	1.084E-01
	2.982E+02		3.624E+00	-2.285E-02	5.222E-04	-3.501E-03	1.226E-05	-1.792E-03	3.212E-06	-2.395E-01	5.734E-02
					2.629E-04		1.394E-05		1.714E-05		1.862E+00
				S Deviation	1.621E-02		3.734E-03		4.140E-03		1.364E+00

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 2	4.482E+02	2.231E-03	6.411E+00	1.432E-01	2.049E-02	1.414E-02	2.000E-04	7.093E-04	5.031E-07	2.110E-04	4.452E-08	-7.026E-05	4.936E-09
	4.232E+02	2.363E-03	5.962E+00	2.005E-02	4.018E-04	-8.540E-03	7.293E-05	-1.274E-03	1.623E-06	-4.932E-04	2.433E-07	3.164E-04	1.001E-07
	3.982E+02	2.512E-03	5.510E+00	-6.607E-02	4.365E-03	-1.398E-02	1.954E-04	-3.471E-04	1.205E-07	-3.889E-05	1.513E-09	-5.834E-04	3.404E-07
	3.732E+02	2.680E-03	5.053E+00	-1.072E-01	1.150E-02	-5.127E-03	2.629E-05	1.691E-03	2.859E-06	1.074E-03	1.154E-06	5.624E-04	3.163E-07
	3.482E+02	2.872E-03	4.587E+00	-9.804E-02	9.611E-03	7.294E-03	5.320E-05	-6.194E-04	3.837E-07	-1.198E-03	1.435E-06	-2.982E-04	8.890E-08
	3.232E+02	3.095E-03	4.115E+00	-2.076E-02	4.311E-04	1.658E-02	2.749E-04	-3.195E-04	1.021E-07	5.302E-04	2.811E-07	8.216E-05	6.751E-09
	2.982E+02	3.354E-03	3.624E+00	1.289E-01	1.662E-02	-1.037E-02	1.076E-04	1.602E-04	2.566E-08	-8.511E-05	7.244E-09	-9.156E-06	8.384E-11
					1.268E-02		2.326E-04		1.872E-06		1.583E-06		8.574E-07
				S Deviation	1.126E-01		1.525E-02		1.368E-03		1.258E-03		9.260E-04

Excel program fitting- 3rd Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 3	4.482E+02		4.428E+00	-8.384E-03	7.028E-05	9.569E-04	9.157E-07	4.099E-03	1.680E-05	-3.845E-01	1.478E-01
	4.232E+02		4.139E+00	-9.184E-04	8.435E-07	-9.092E-04	8.266E-07	3.505E-03	1.228E-05	-3.056E-01	9.339E-02
	3.981E+02		3.848E+00	4.537E-03	2.058E-05	-1.057E-03	1.116E-06	2.780E-03	7.731E-06	-2.396E-01	5.739E-02
	3.732E+02		3.555E+00	7.689E-03	5.913E-05	2.294E-04	5.263E-08	2.597E-03	6.747E-06	-1.845E-01	3.403E-02
	3.482E+02		3.257E+00	6.258E-03	3.916E-05	6.631E-04	4.397E-07	1.626E-03	2.643E-06	-1.402E-01	1.967E-02
	3.231E+02		2.956E+00	1.163E-03	1.354E-06	1.168E-03	1.365E-06	1.745E-03	3.047E-06	-1.037E-01	1.075E-02
	2.981E+02		2.648E+00	-1.035E-02	1.070E-04	-1.009E-03	1.018E-06	1.159E-03	1.344E-06	-7.526E-02	5.664E-03
					5.967E-05		1.433E-06		1.687E-05		7.375E-02
				S Deviation	7.725E-03		1.197E-03		4.107E-03		2.716E-01

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 3	4.482E+02	2.231E-03	4.428E+00	9.428E-02	8.889E-03	8.748E-03	7.652E-05	6.576E-04	4.325E-07	6.063E-05	3.675E-09	-2.408E-05	5.798E-10
	4.232E+02	2.363E-03	4.139E+00	1.352E-02	1.828E-04	-5.445E-03	2.965E-05	-1.071E-03	1.146E-06	-1.354E-04	1.832E-08	1.084E-04	1.174E-08
	3.981E+02	2.512E-03	3.848E+00	-4.316E-02	1.863E-03	-8.615E-03	7.422E-05	-4.052E-04	1.642E-07	-3.591E-05	1.289E-09	-1.998E-04	3.994E-08
	3.732E+02	2.680E-03	3.555E+00	-7.073E-02	5.003E-03	-3.021E-03	9.129E-06	1.085E-03	1.178E-06	3.467E-04	1.202E-07	1.927E-04	3.713E-08
	3.482E+02	2.872E-03	3.257E+00	-6.475E-02	4.193E-03	5.086E-03	2.587E-05	3.201E-04	1.024E-07	-3.730E-04	1.392E-07	-1.022E-04	1.044E-08
	3.231E+02	3.095E-03	2.956E+00	-1.543E-02	2.382E-04	9.324E-03	8.693E-05	-8.548E-04	7.307E-07	1.630E-04	2.657E-08	2.815E-05	7.924E-10
	2.981E+02	3.354E-03	2.648E+00	8.628E-02	7.444E-03	-6.075E-03	3.691E-05	2.678E-04	7.173E-08	-2.600E-05	6.762E-10	-3.138E-06	9.844E-12
					5.563E-03		8.481E-05		1.275E-06		1.549E-07		1.006E-07
				S Deviation	7.458E-02		9.209E-03		1.129E-03		3.936E-04		3.172E-04

Excel program fitting- 4th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 4	4.482E+02		3.038E+00	-3.863E-03	1.492E-05	4.405E-04	1.940E-07	-5.959E-04	3.551E-07	5.076E-01	2.577E-01
	4.232E+02		2.849E+00	-4.705E-04	2.214E-07	-4.773E-04	2.278E-07	-5.740E-04	3.295E-07	4.037E-01	1.630E-01
	3.982E+02		2.660E+00	2.094E-03	4.386E-06	-4.992E-04	2.492E-07	-5.094E-04	2.595E-07	3.165E-01	1.002E-01
	3.732E+02		2.469E+00	3.681E-03	1.355E-05	2.264E-04	5.124E-08	-1.287E-04	1.656E-08	2.445E-01	5.980E-02
	3.482E+02		2.276E+00	2.824E-03	7.977E-06	2.324E-04	5.401E-08	-4.772E-04	2.277E-07	1.851E-01	3.425E-02
	3.231E+02		2.081E+00	4.615E-04	2.130E-07	4.579E-04	2.097E-07	-1.938E-04	3.755E-08	1.377E-01	1.896E-02
	2.982E+02		1.884E+00	-4.728E-03	2.235E-05	-4.199E-04	1.764E-07	-1.798E-04	3.232E-08	9.979E-02	9.957E-03
					1.273E-05		**2.906E-07**		**4.194E-07**		**3.219E-01**
				S Deviation	**3.567E-03**		**5.390E-04**		**6.476E-04**		**5.674E-01**

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 4	4.482E+02	2.231E-03	3.038E+00	6.292E-02	3.959E-03	5.786E-03	3.348E-05	4.637E-04	2.150E-07	4.313E-05	1.860E-09	-1.682E-05	2.830E-10
	4.232E+02	2.363E-03	2.849E+00	9.030E-03	8.155E-05	-3.634E-03	1.321E-05	-7.557E-04	5.711E-07	-9.679E-05	9.369E-09	7.574E-05	5.736E-09
	3.982E+02	2.512E-03	2.660E+00	-2.876E-02	8.271E-04	-5.684E-03	3.231E-05	-2.838E-04	8.055E-08	-2.363E-05	5.585E-10	-1.396E-04	1.950E-08
	3.732E+02	2.680E-03	2.469E+00	-4.717E-02	2.225E-03	-1.937E-03	3.754E-06	7.640E-04	5.837E-07	2.437E-04	5.937E-08	1.346E-04	1.812E-08
	3.482E+02	2.872E-03	2.276E+00	-4.329E-02	1.874E-03	3.361E-03	1.130E-05	2.251E-04	5.068E-08	-2.631E-04	6.923E-08	-7.137E-05	5.093E-09
	3.231E+02	3.095E-03	2.081E+00	-1.044E-02	1.090E-04	6.093E-03	3.713E-05	-6.020E-04	3.624E-07	1.152E-04	1.326E-08	1.967E-05	3.869E-10
	2.982E+02	3.354E-03	1.884E+00	5.770E-02	3.330E-03	-3.985E-03	1.588E-05	1.887E-04	3.560E-08	-1.839E-05	3.381E-10	-2.193E-06	4.810E-12
					2.481E-03		**3.676E-05**		**6.330E-07**		**7.700E-08**		**4.913E-08**
				S Deviation	**4.981E-02**		**6.063E-03**		**7.956E-04**		**2.775E-04**		**2.217E-04**

Excel program fitting- 5th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 5	4.482E+02		2.074E+00	-1.986E-03	3.943E-06	1.362E-04	1.854E-08	-2.698E-03	7.278E-06	-4.913E-02	2.414E-03
	4.232E+02		1.950E+00	-1.714E-04	2.939E-08	-1.681E-04	2.827E-08	-2.334E-03	5.449E-06	-3.910E-02	1.529E-03
	3.981E+02		1.825E+00	1.204E-03	1.449E-06	-6.432E-05	4.137E-09	-1.849E-03	3.418E-06	-3.053E-02	9.320E-04
	3.731E+02		1.699E+00	1.743E-03	3.039E-06	5.129E-05	2.631E-09	-1.516E-03	2.297E-06	-2.352E-02	5.534E-04
	3.482E+02		1.573E+00	1.256E-03	1.578E-06	-1.258E-05	1.584E-10	-1.404E-03	1.972E-06	-1.799E-02	3.235E-04
	3.232E+02		1.445E+00	2.150E-04	4.624E-08	2.171E-04	4.712E-08	-9.194E-04	8.454E-07	-1.315E-02	1.729E-04
	2.982E+02		1.317E+00	-2.261E-03	5.112E-06	-1.411E-04	1.991E-08	-8.211E-04	6.742E-07	-9.604E-03	9.224E-05
					3.039E-06		3.019E-08		7.311E-06		3.008E-03
				S Deviation	1.743E-03		1.738E-04		2.704E-03		5.485E-02

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 5	4.482E+02	2.231E-03	2.074E+00	4.193E-02	1.758E-03	3.733E-03	1.394E-05	2.656E-04	7.052E-08	4.231E-05	1.790E-09	-1.960E-06	3.842E-12
	4.232E+02	2.363E-03	1.950E+00	6.121E-03	3.747E-05	-2.344E-03	5.496E-06	-4.685E-04	2.195E-07	-1.186E-04	1.407E-08	8.825E-06	7.789E-11
	3.981E+02	2.512E-03	1.825E+00	-1.902E-02	3.616E-04	-3.588E-03	1.287E-05	-6.860E-05	4.706E-09	6.948E-05	4.828E-09	-1.627E-05	2.648E-10
	3.731E+02	2.680E-03	1.699E+00	-3.163E-02	1.000E-03	-1.387E-03	1.923E-06	3.725E-04	1.387E-07	9.619E-05	9.253E-09	1.570E-05	2.464E-10
	3.482E+02	2.872E-03	1.573E+00	-2.904E-02	8.431E-04	2.152E-03	4.630E-06	1.092E-04	1.193E-08	-1.500E-04	2.249E-08	-8.324E-06	6.929E-11
	3.232E+02	3.095E-03	1.445E+00	-7.001E-03	4.901E-05	4.055E-03	1.644E-05	-3.079E-04	9.480E-08	7.280E-05	5.300E-09	2.293E-06	5.258E-12
	2.982E+02	3.354E-03	1.317E+00	3.862E-02	1.492E-03	-2.621E-03	6.870E-06	9.770E-05	9.544E-09	-1.221E-05	1.491E-10	-2.556E-07	6.533E-14
					1.108E-03		1.554E-05		1.832E-07		2.894E-08		6.675E-10
				S Deviation	3.329E-02		3.942E-03		4.281E-04		1.701E-04		2.584E-05

Excel program fitting- 6th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 6	4.482E+02		1.411E+00	-9.552E-04	9.124E-07	6.470E-05	4.186E-09	-2.126E-03	4.521E-06	6.621E-02	4.384E-03
	4.232E+02		1.328E+00	-8.858E-05	7.846E-09	-8.252E-05	6.810E-09	-1.845E-03	3.405E-06	5.254E-02	2.761E-03
	3.981E+02		1.245E+00	5.937E-04	3.525E-07	-9.138E-06	8.350E-11	-1.470E-03	2.162E-06	4.119E-02	1.697E-03
	3.731E+02		1.162E+00	8.596E-04	7.390E-07	5.357E-05	2.870E-09	-1.187E-03	1.408E-06	3.176E-02	1.009E-03
	3.482E+02		1.078E+00	5.612E-04	3.150E-07	-4.279E-05	1.831E-09	-1.095E-03	1.199E-06	2.391E-02	5.719E-04
	3.232E+02		9.944E-01	9.820E-05	9.644E-09	1.016E-04	1.033E-08	-7.492E-04	5.613E-07	1.785E-02	3.187E-04
	2.982E+02		9.098E-01	-1.069E-03	1.143E-06	-5.263E-05	2.770E-09	-6.415E-04	4.115E-07	1.285E-02	1.652E-04
					6.958E-07		7.220E-09		4.556E-06		5.453E-03
				S Deviation	8.341E-04		8.497E-05		2.135E-03		7.385E-02

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 6	4.482E+02	2.231E-03	1.411E+00	2.815E-02	7.926E-04	2.506E-03	6.280E-06	1.818E-04	3.304E-08	2.857E-05	8.165E-10	-2.013E-06	4.052E-12
	4.232E+02	2.363E-03	1.328E+00	4.111E-03	1.690E-05	-1.576E-03	2.484E-06	-3.190E-04	1.018E-07	-7.897E-05	6.236E-09	9.058E-06	8.205E-11
	3.981E+02	2.512E-03	1.245E+00	-1.277E-02	1.631E-04	-2.411E-03	5.814E-06	-5.220E-05	2.725E-09	4.254E-05	1.809E-09	-1.670E-05	2.790E-10
	3.731E+02	2.680E-03	1.162E+00	-2.122E-02	4.504E-04	-9.180E-04	8.428E-07	2.612E-04	6.825E-08	7.169E-05	5.139E-09	1.611E-05	2.597E-10
	3.482E+02	2.872E-03	1.078E+00	-1.950E-02	3.802E-04	1.440E-03	2.075E-06	7.144E-05	5.104E-09	-1.064E-04	1.131E-08	-8.547E-06	7.306E-11
	3.232E+02	3.095E-03	9.944E-01	-4.710E-03	2.219E-05	2.714E-03	7.367E-06	-2.101E-04	4.415E-08	5.105E-05	2.606E-09	2.355E-06	5.545E-12
	2.982E+02	3.354E-03	9.098E-01	2.594E-02	6.728E-04	-1.755E-03	3.081E-06	6.687E-05	4.471E-09	-8.517E-06	7.254E-11	-2.622E-07	6.874E-14
					4.996E-04		6.986E-06		8.650E-08		1.400E-08		7.035E-10
				S Deviation	2.235E-02		2.643E-03		2.941E-04		1.183E-04		2.652E-05

Excel program fitting- 7th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 7	4.481E+02		9.574E-01	-4.647E-04	2.160E-07	2.962E-05	8.773E-10	2.521E-03	6.357E-06	1.560E-01	2.435E-02
	4.232E+02		9.022E-01	-5.621E-05	3.160E-09	-4.743E-05	2.249E-09	2.054E-03	4.221E-06	1.241E-01	1.539E-02
	3.982E+02		8.470E-01	3.264E-04	1.065E-07	4.349E-05	1.891E-09	1.794E-03	3.220E-06	9.740E-02	9.486E-03
	3.731E+02		7.915E-01	4.264E-04	1.818E-07	4.563E-05	2.083E-09	1.484E-03	2.203E-06	7.519E-02	5.654E-03
	3.482E+02		7.357E-01	2.250E-04	5.060E-08	-5.984E-05	3.580E-09	1.106E-03	1.223E-06	5.695E-02	3.244E-03
	3.232E+02		6.799E-01	3.438E-05	1.182E-09	3.951E-05	1.561E-09	9.707E-04	9.422E-07	4.242E-02	1.800E-03
	2.982E+02		6.237E-01	-4.913E-04	2.414E-07	-2.414E-06	5.828E-12	7.332E-04	5.376E-07	3.073E-02	9.445E-04
					2.002E-07		**3.062E-09**		**6.235E-06**		**3.044E-02**
				S Deviation	**4.474E-04**		**5.533E-05**		**2.497E-03**		**1.745E-01**

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 7	4.481E+02	2.231E-03	9.574E-01	1.894E-02	3.588E-04	1.679E-03	2.821E-06	1.284E-04	1.649E-08	2.463E-05	6.067E-10	-2.461E-07	6.055E-14
	4.232E+02	2.363E-03	9.022E-01	2.754E-03	7.582E-06	-1.072E-03	1.149E-06	-2.331E-04	5.435E-08	-7.051E-05	4.971E-09	1.108E-06	1.227E-12
	3.982E+02	2.512E-03	8.470E-01	-8.560E-03	7.328E-05	-1.592E-03	2.534E-06	-1.813E-05	3.286E-10	4.613E-05	2.128E-09	-2.042E-06	4.169E-12
	3.731E+02	2.680E-03	7.915E-01	-1.428E-02	2.039E-04	-6.112E-04	3.735E-07	1.757E-04	3.087E-08	4.723E-05	2.230E-09	1.968E-06	3.875E-12
	3.482E+02	2.872E-03	7.357E-01	-1.314E-02	1.727E-04	9.533E-04	9.087E-07	3.988E-05	1.590E-09	-8.064E-05	6.502E-09	-1.044E-06	1.090E-12
	3.232E+02	3.095E-03	6.799E-01	-3.183E-03	1.013E-05	1.814E-03	3.290E-06	-1.371E-04	1.880E-08	3.991E-05	1.592E-09	2.877E-07	8.277E-14
	2.982E+02	3.354E-03	6.237E-01	1.747E-02	3.051E-04	-1.172E-03	1.372E-06	4.435E-05	1.967E-09	-6.749E-06	4.555E-11	-3.202E-08	1.025E-15
					2.263E-04		**3.112E-06**		**4.147E-08**		**9.038E-09**		**1.051E-11**
				S Deviation	**1.504E-02**		**1.764E-03**		**2.036E-04**		**9.507E-05**		**3.241E-06**

Excel program fitting- 8th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 7	4.482E+02		6.486E-01	-3.093E-01	9.568E-02	-3.088E-01	9.538E-02	2.138E-03	4.571E-06	-6.555E-02	4.297E-03
	4.232E+02		6.117E-01	-2.906E-01	8.446E-02	-2.906E-01	8.445E-02	1.773E-03	3.143E-06	-5.223E-02	2.728E-03
	3.981E+02		5.747E-01	-2.720E-01	7.396E-02	-2.722E-01	7.412E-02	1.525E-03	2.326E-06	-4.096E-02	1.678E-03
	3.731E+02		5.375E-01	-2.535E-01	6.427E-02	-2.539E-01	6.446E-02	1.242E-03	1.543E-06	-3.168E-02	1.004E-03
	3.482E+02		5.002E-01	-2.352E-01	5.533E-02	-2.355E-01	5.546E-02	9.405E-04	8.846E-07	-2.414E-02	5.826E-04
	3.232E+02		4.630E-01	-2.168E-01	4.702E-02	-2.168E-01	4.702E-02	8.469E-04	7.173E-07	-1.788E-02	3.198E-04
	2.982E+02		4.255E-01	-1.987E-01	3.949E-02	-1.982E-01	3.929E-02	6.142E-04	3.773E-07	-1.304E-02	1.701E-04
					1.151E-01		1.150E-01		4.520E-06		5.390E-03
				S Deviation	3.392E-01		3.392E-01		2.126E-03		7.341E-02

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 7	4.482E+02	2.231E-03	6.486E-01	-2.899E-01	8.405E-02	-3.072E-01	9.436E-02	6.717E-05	4.511E-09	1.821E-05	3.314E-10	-3.635E-06	1.321E-11
	4.232E+02	2.363E-03	6.117E-01	-2.878E-01	8.283E-02	-2.916E-01	8.505E-02	-1.389E-04	1.928E-08	-4.713E-05	2.221E-09	-2.495E-06	6.227E-12
	3.981E+02	2.512E-03	5.747E-01	-2.809E-01	7.888E-02	-2.739E-01	7.501E-02	-6.989E-06	4.885E-11	3.275E-05	1.072E-09	-5.145E-06	2.647E-11
	3.731E+02	2.680E-03	5.375E-01	-2.682E-01	7.194E-02	-2.546E-01	6.480E-02	9.607E-05	9.229E-09	3.409E-05	1.162E-09	-1.768E-06	3.127E-12
	3.482E+02	2.872E-03	5.002E-01	-2.486E-01	6.180E-02	-2.345E-01	5.499E-02	3.347E-06	1.121E-11	-5.444E-05	2.964E-09	-4.304E-06	1.852E-11
	3.232E+02	3.095E-03	4.630E-01	-2.201E-01	4.843E-02	-2.151E-01	4.625E-02	-7.048E-05	4.968E-09	2.881E-05	8.300E-10	-3.182E-06	1.012E-11
	2.982E+02	3.354E-03	4.255E-01	-1.808E-01	3.267E-02	-1.994E-01	3.976E-02	1.775E-05	3.152E-10	-3.387E-06	1.147E-11	-3.450E-06	1.190E-11
					9.212E-02		1.151E-01		1.279E-08		4.296E-09		8.959E-11
				S Deviation	3.035E-01		3.392E-01		1.131E-04		6.555E-05		9.465E-06

Excel program fitting- 9th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 7	4.482E+02		4.389E-01	-5.190E-01	2.694E-01	-5.185E-01	2.689E-01	4.891E-06	2.392E-11	1.374E-06	1.887E-12
	4.232E+02		4.141E-01	-4.882E-01	2.384E-01	-4.882E-01	2.384E-01	-1.820E-05	3.312E-10	-2.745E-05	7.537E-10
	3.982E+02		3.892E-01	-4.574E-01	2.093E-01	-4.577E-01	2.095E-01	2.668E-05	7.120E-10	2.289E-05	5.240E-10
	3.731E+02		3.643E-01	-4.268E-01	1.821E-01	-4.272E-01	1.825E-01	3.533E-06	1.248E-11	3.297E-06	1.087E-11
	3.482E+02		3.393E-01	-3.962E-01	1.570E-01	-3.965E-01	1.572E-01	-3.662E-05	1.341E-09	-3.957E-05	1.566E-09
	3.232E+02		3.143E-01	-3.655E-01	1.336E-01	-3.655E-01	1.336E-01	3.219E-05	1.036E-09	2.462E-05	6.062E-10
	2.982E+02		2.892E-01	-3.350E-01	1.122E-01	-3.345E-01	1.119E-01	-8.032E-06	6.451E-11	-9.005E-06	8.109E-11
					3.255E-01		3.255E-01		1.174E-09		1.772E-09
				S Deviation	5.705E-01		5.705E-01		3.426E-05		4.209E-05

	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 7	4.482E+02	2.231E-03	4.389E-01	-4.996E-01	2.496E-01	-5.169E-01	2.671E-01	5.162E-05	2.664E-09	1.163E-05	1.353E-10	-2.224E-06	4.947E-12
	4.232E+02	2.363E-03	4.141E-01	-4.854E-01	2.356E-01	-4.892E-01	2.394E-01	-9.420E-05	8.874E-09	-3.942E-05	1.554E-09	-8.981E-06	8.065E-11
	3.981E+02	2.512E-03	3.892E-01	-4.663E-01	2.175E-01	-4.594E-01	2.110E-01	1.153E-05	1.328E-10	3.128E-05	9.787E-10	6.743E-06	4.546E-11
	3.732E+02	2.680E-03	3.643E-01	-4.415E-01	1.949E-01	-4.278E-01	1.830E-01	5.868E-05	3.443E-09	9.931E-06	9.862E-11	-1.328E-05	1.764E-10
	3.482E+02	2.872E-03	3.393E-01	-4.095E-01	1.677E-01	-3.954E-01	1.564E-01	1.359E-05	1.847E-10	-3.235E-05	1.047E-09	1.754E-06	3.077E-12
	3.232E+02	3.095E-03	3.143E-01	-3.687E-01	1.360E-01	-3.637E-01	1.323E-01	-4.414E-05	1.948E-09	1.574E-05	2.477E-10	-4.891E-06	2.392E-11
	2.982E+02	3.354E-03	2.892E-01	-3.170E-01	1.005E-01	-3.357E-01	1.127E-01	1.731E-05	2.996E-10	-3.947E-06	1.558E-11	-3.297E-06	1.087E-11
					2.604E-01		3.255E-01		5.849E-09		2.038E-09		3.453E-10
				S Deviation	5.103E-01		5.705E-01		7.648E-05		4.515E-05		1.858E-05

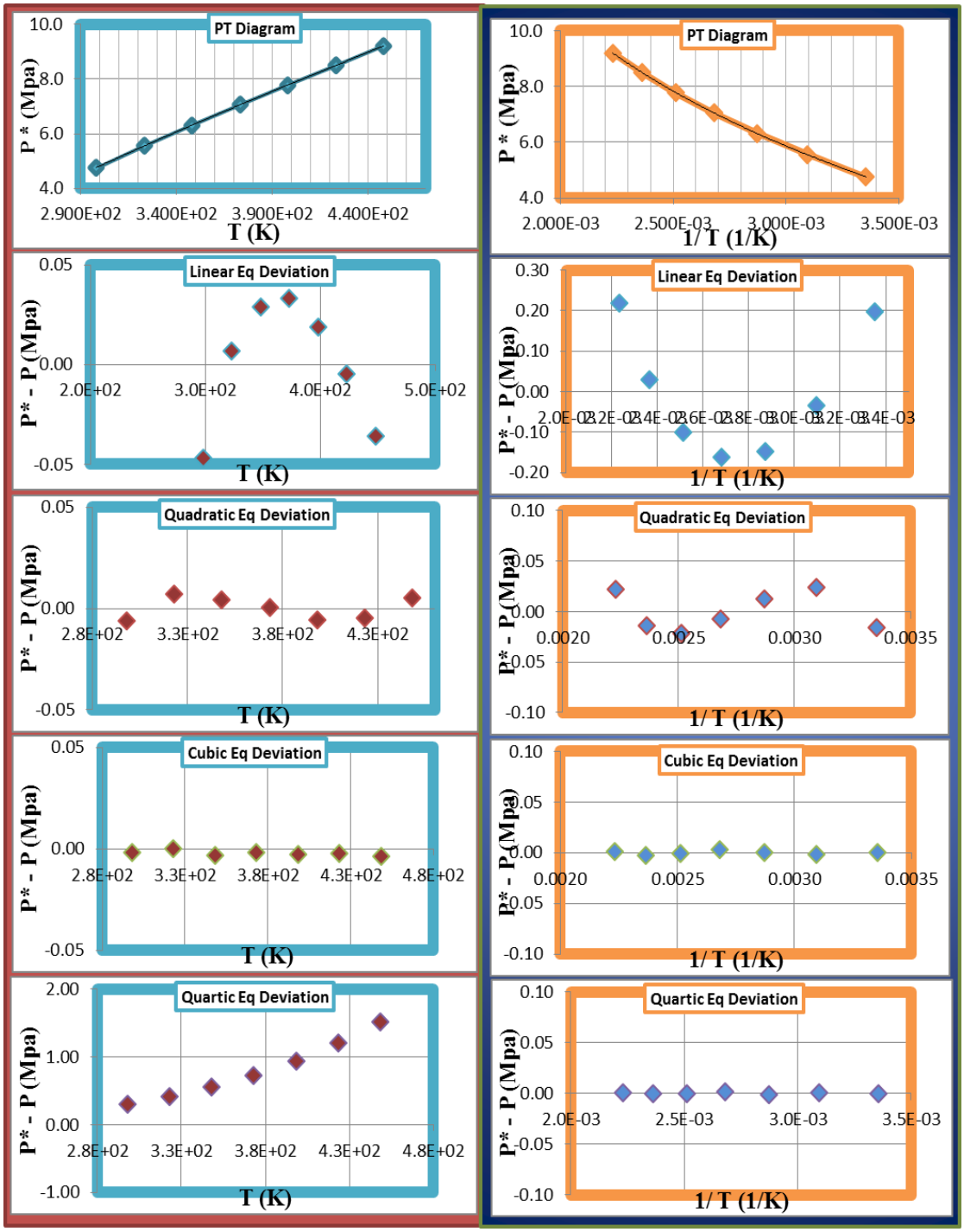
Excel program fitting- 10th Isocohre of (PT) & (P1/T) study tables

	T/K		P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2
I 7	4.482E+02		2.967E-01	-6.612E-01	4.372E-01	-6.607E-01	4.365E-01	3.454E-06	1.193E-11	4.826E-06	2.329E-11
	4.232E+02		2.800E-01	-6.222E-01	3.872E-01	-6.222E-01	3.872E-01	-1.540E-05	2.371E-10	-1.680E-05	2.822E-10
	3.981E+02		2.634E-01	-5.833E-01	3.403E-01	-5.836E-01	3.406E-01	2.012E-05	4.049E-10	2.093E-05	4.382E-10
	3.732E+02		2.466E-01	-5.445E-01	2.965E-01	-5.449E-01	2.969E-01	7.583E-07	5.750E-13	2.948E-06	8.691E-12
	3.482E+02		2.298E-01	-5.057E-01	2.557E-01	-5.060E-01	2.560E-01	-2.493E-05	6.213E-10	-2.413E-05	5.825E-10
	3.232E+02		2.130E-01	-4.668E-01	2.179E-01	-4.668E-01	2.179E-01	2.050E-05	4.204E-10	1.906E-05	3.634E-10
	2.982E+02		1.962E-01	-4.280E-01	1.832E-01	-4.276E-01	1.828E-01	-5.693E-06	3.241E-11	-4.382E-06	1.920E-11
					5.295E-01		5.295E-01		5.762E-10		8.587E-10
				S Deviation	7.277E-01		7.276E-01		2.400E-05		2.930E-05

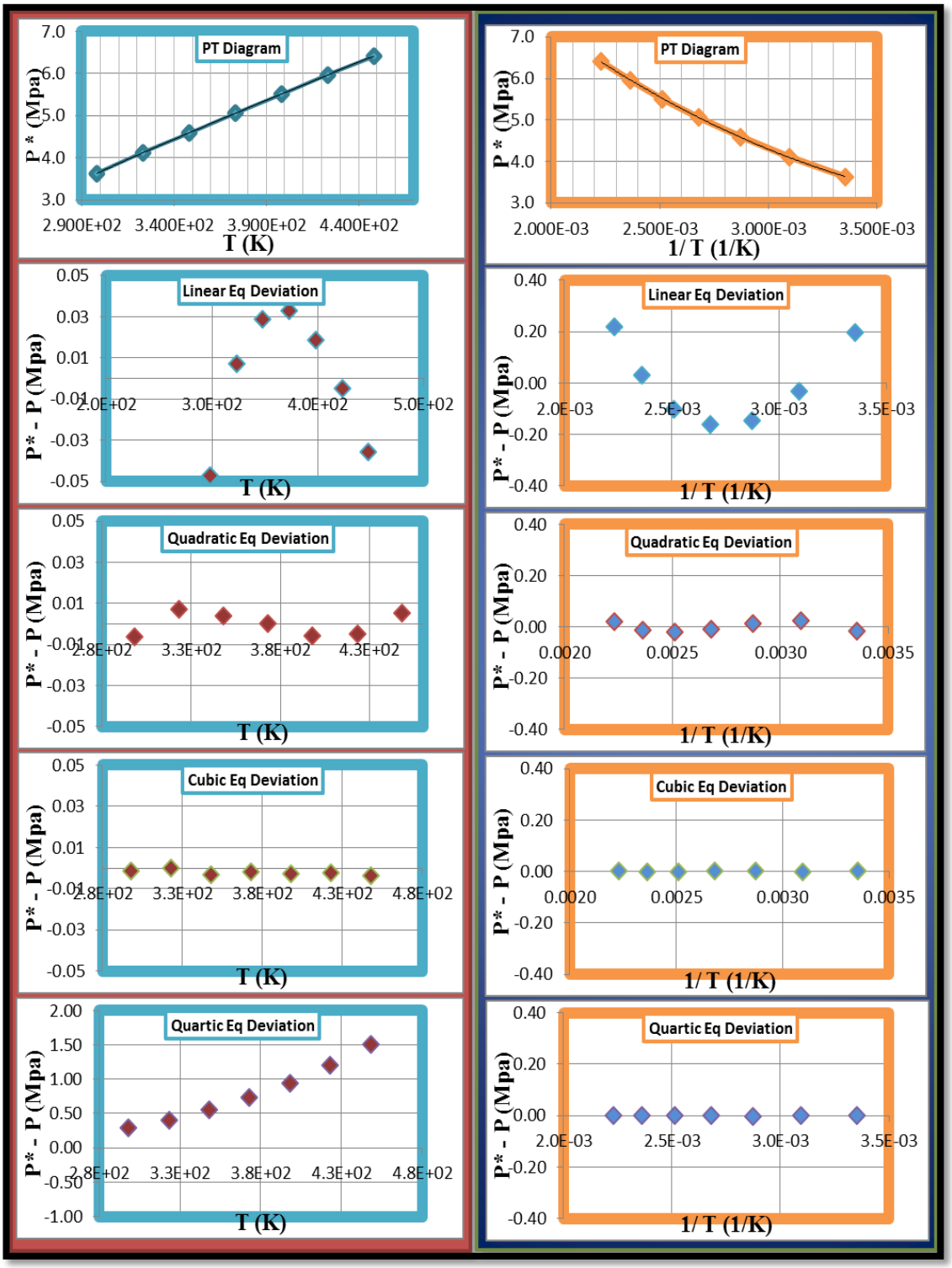
	T/K	1/T	P*/MPa	Linear (dev)	Linear (dev)^2	Quadratic (dev)	Quadratic (dev)^2	Cubic (dev)	Cubic (dev)^2	Quartic (dev)	Quartic (dev)^2	Quintic (dev)	Quintic (dev)^2
I 7	4.482E+02	2.231E-03	2.967E-01	-6.418E-01	4.119E-01	-6.590E-01	4.343E-01	3.094E-05	9.573E-10	8.455E-06	7.149E-11	4.915E-06	2.416E-11
	4.232E+02	2.363E-03	2.800E-01	-6.194E-01	3.837E-01	-6.233E-01	3.885E-01	-6.823E-05	4.655E-09	-2.666E-05	7.108E-10	1.504E-06	2.262E-12
	3.981E+02	2.512E-03	2.634E-01	-5.922E-01	3.507E-01	-5.852E-01	3.425E-01	2.734E-06	7.476E-12	2.063E-05	4.256E-10	9.442E-06	8.915E-11
	3.732E+02	2.680E-03	2.466E-01	-5.592E-01	3.127E-01	-5.455E-01	2.976E-01	3.798E-05	1.442E-09	9.571E-06	9.160E-11	-6.680E-07	4.463E-13
	3.482E+02	2.872E-03	2.298E-01	-5.190E-01	2.694E-01	-5.049E-01	2.550E-01	2.644E-06	6.992E-12	-2.386E-05	5.695E-10	6.923E-06	4.793E-11
	3.232E+02	3.095E-03	2.130E-01	-4.700E-01	2.209E-01	-4.650E-01	2.163E-01	-3.305E-05	1.093E-09	1.196E-05	1.430E-10	3.568E-06	1.273E-11
	2.982E+02	3.354E-03	1.962E-01	-4.101E-01	1.682E-01	-4.287E-01	1.838E-01	7.352E-06	5.405E-11	-2.467E-06	6.085E-12	4.373E-06	1.912E-11
					4.235E-01		5.295E-01		2.739E-09		1.009E-09		1.958E-10
				S Deviation	6.508E-01		7.277E-01		5.233E-05		3.177E-05		1.399E-05

APPENDIX B: EXPERIMENTAL DATA FIGURES

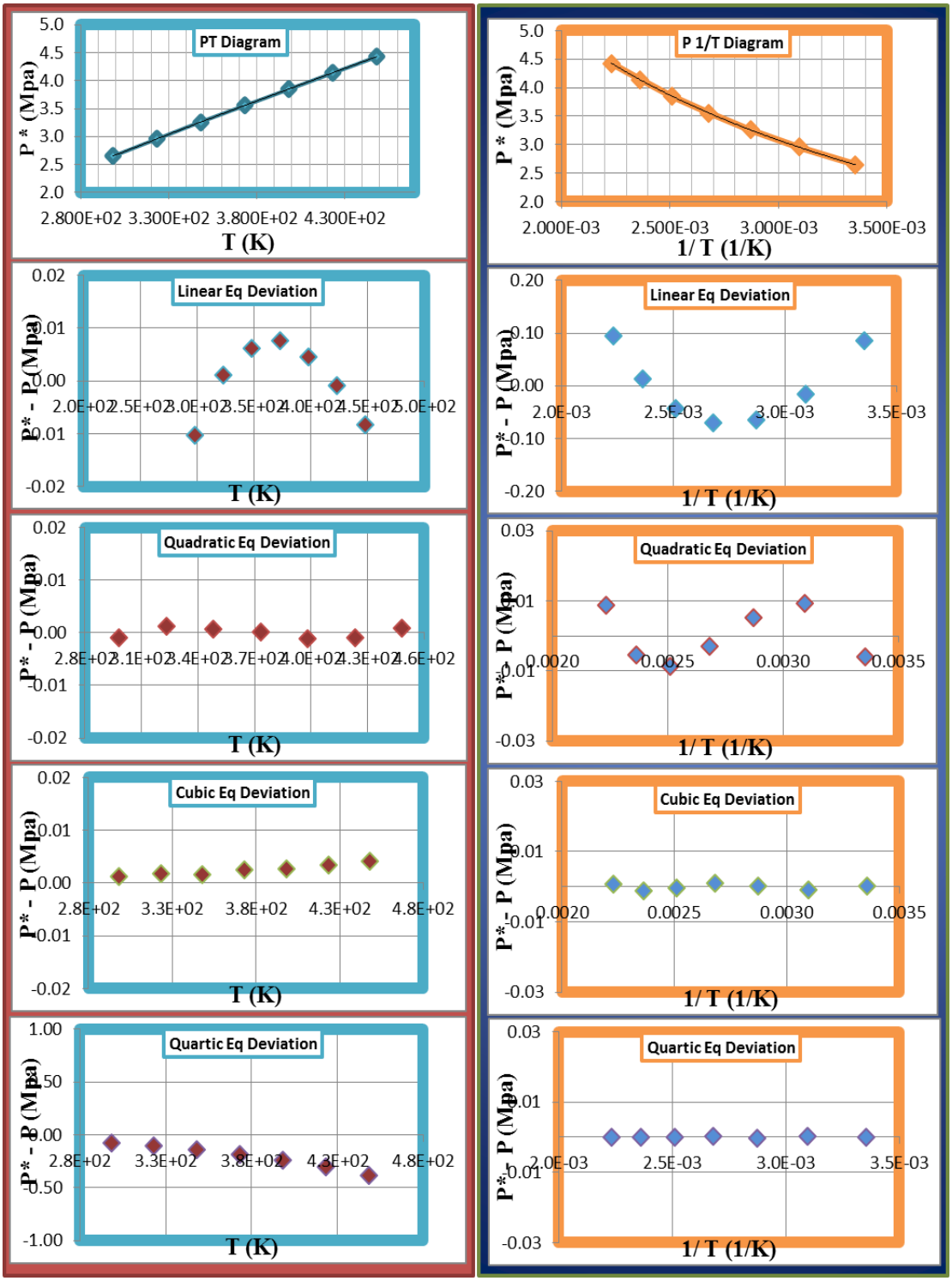
Excel program fitting- 1st Isocohre of (PT) & (P1/T) studies



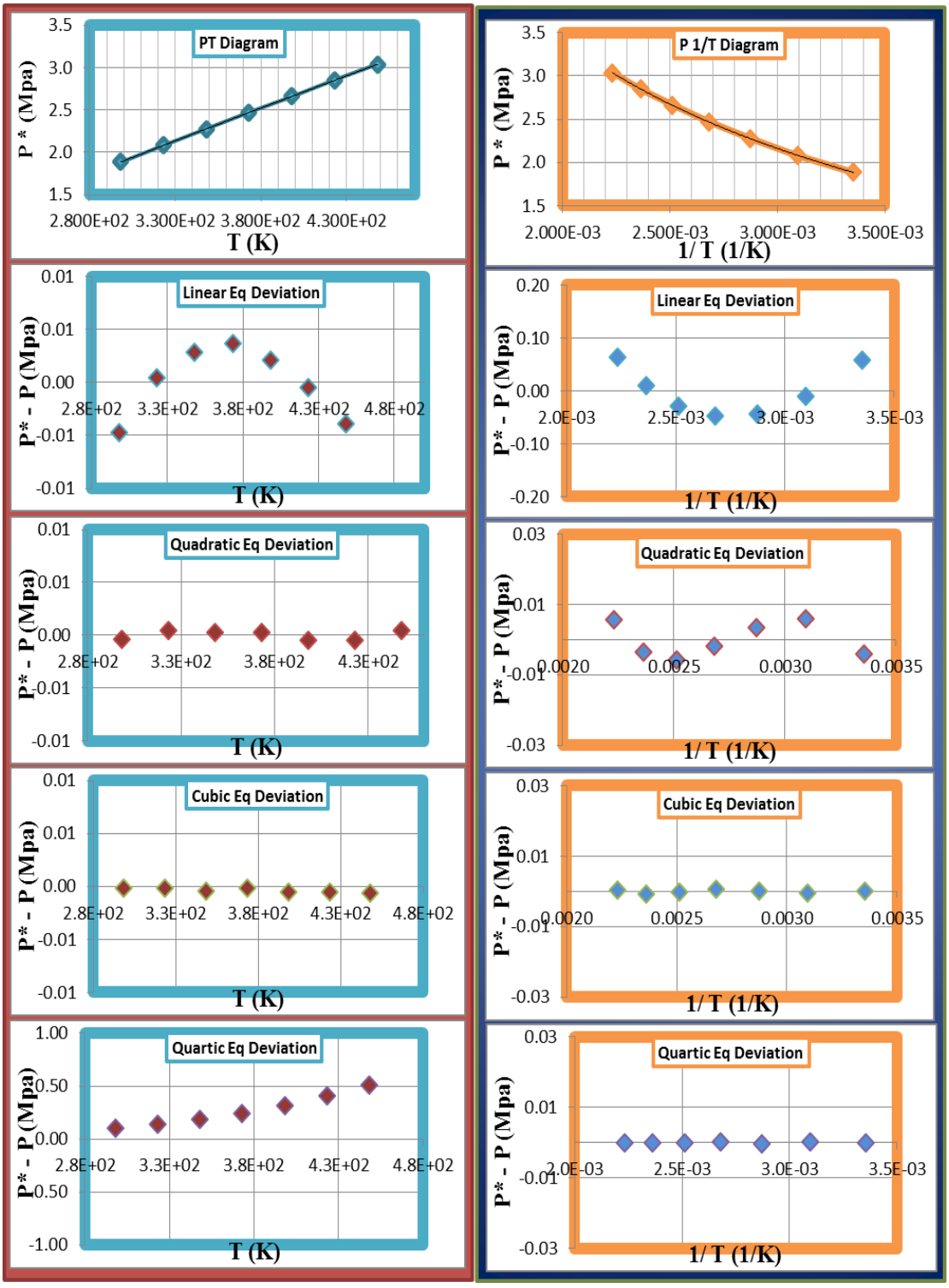
Excel program fitting- 2nd Isocohre of (PT) & (P1/T) studies



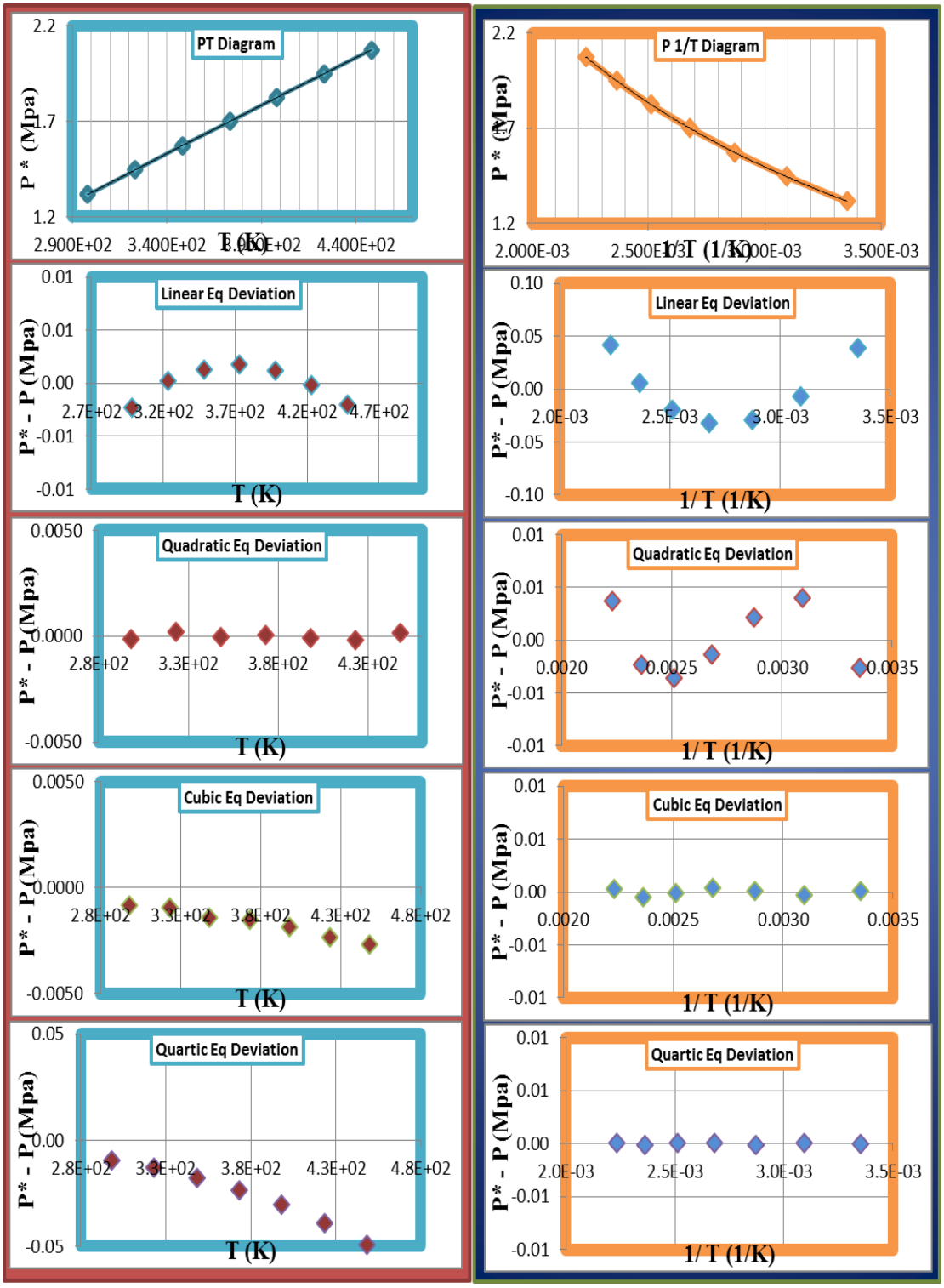
Excel program fitting- 3rd Isocohre of (PT) & (P1/T) studies



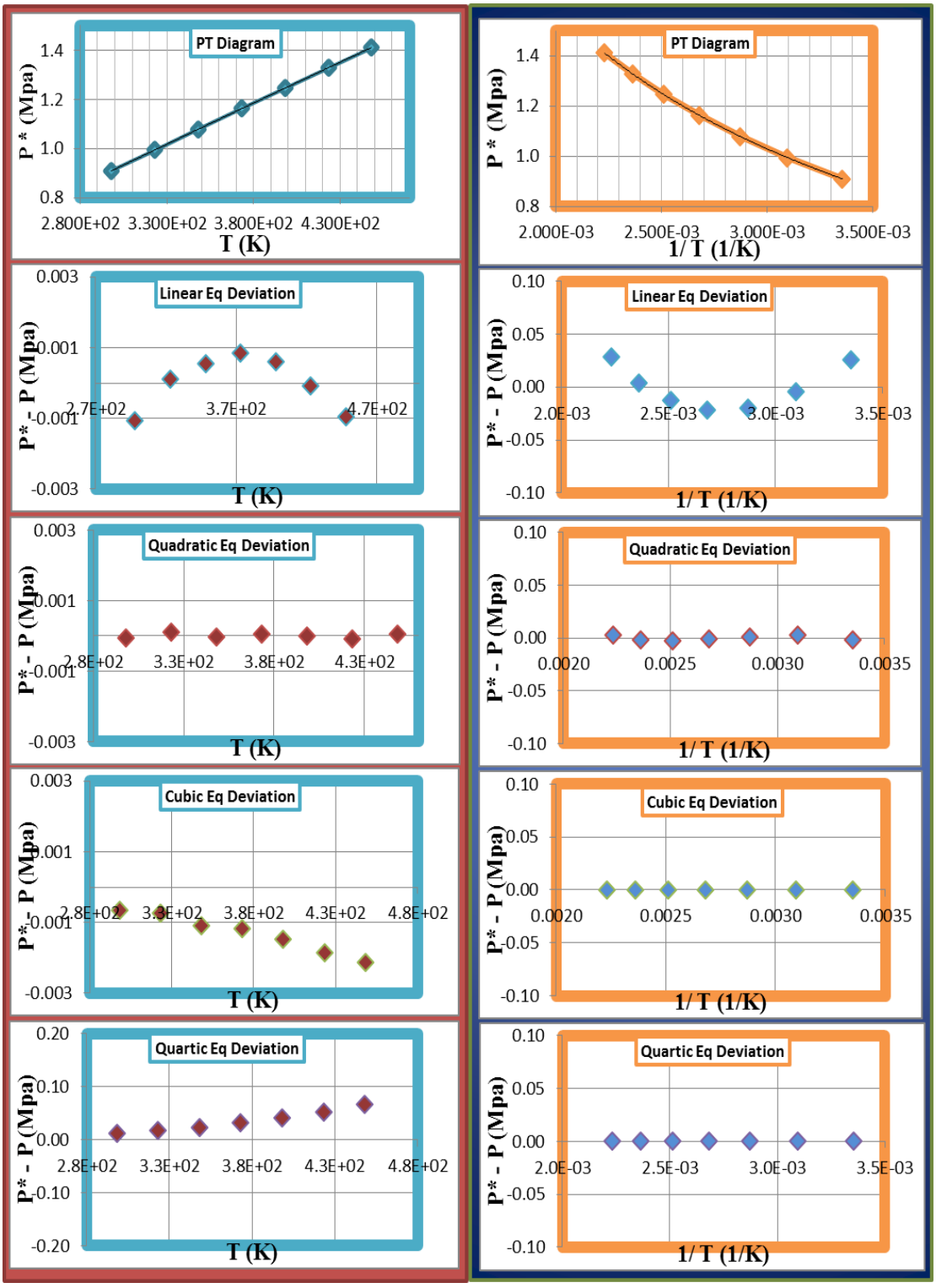
Excel program fitting- 4th Isocohre of (PT) & (P1/T) studies



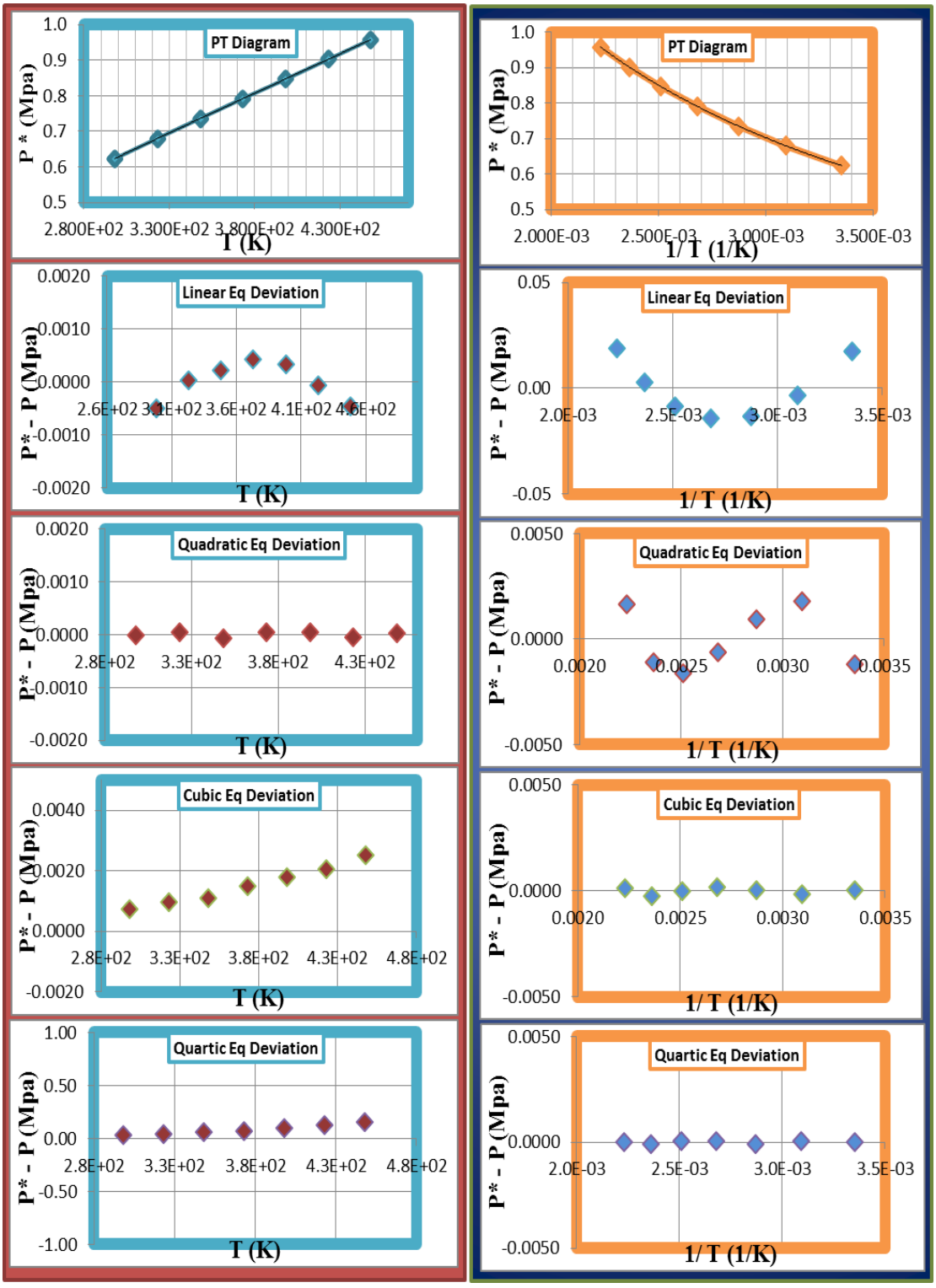
Excel program fitting- 5th Isocohre of (PT) & (P1/T) studies



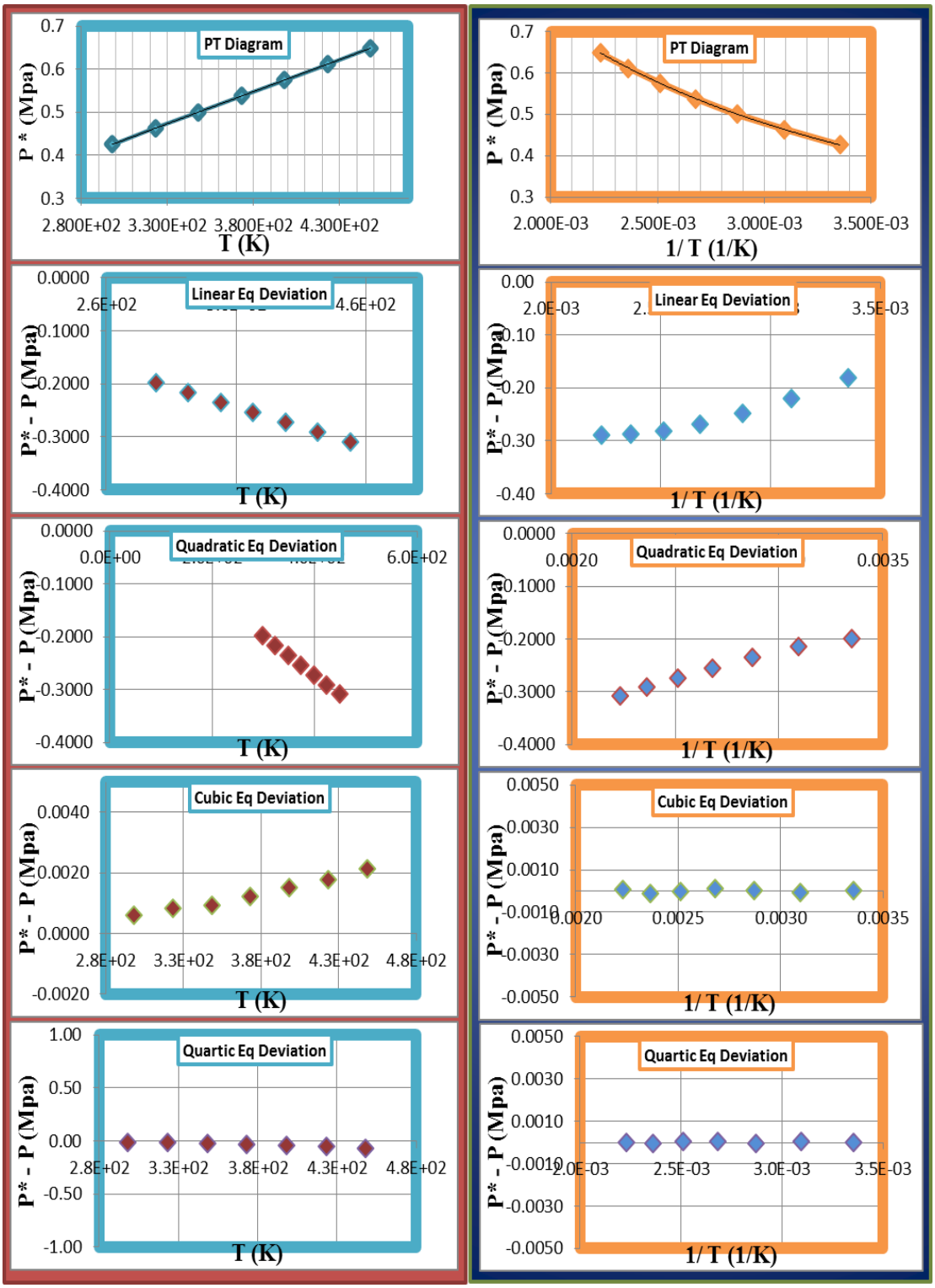
Excel program fitting- 6th Isocohre of (PT) & (P1/T) studies



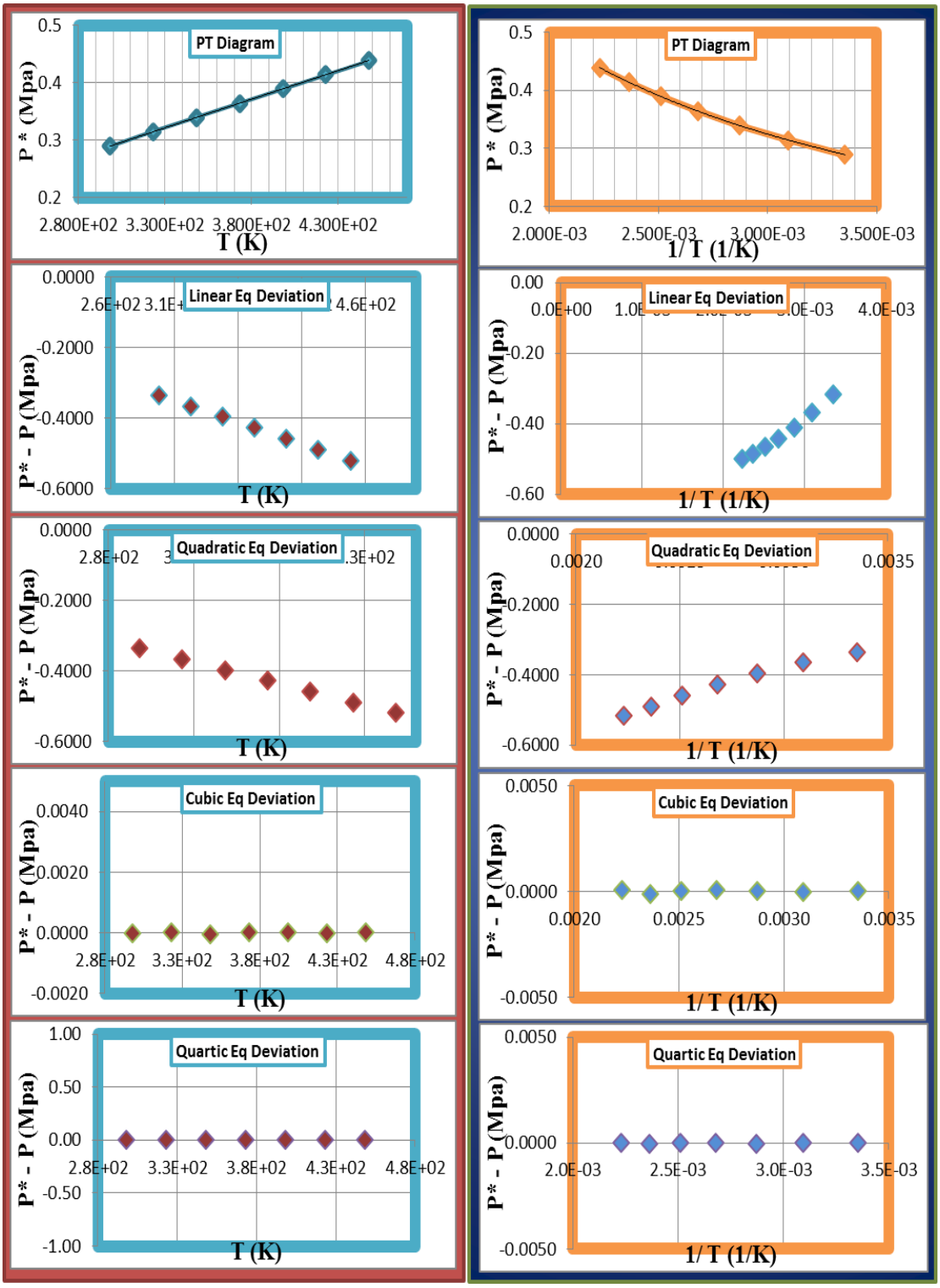
Excel program fitting- 7th Isocohre of (PT) & (P1/T) studies



Excel program fitting- 8th Isocohre of (PT) & (P1/T) studies



Excel program fitting- 9th Isocohre of (PT) & (P1/T) studies



Excel program fitting- 10th Isocohre of (PT) & (P1/T) studies